REMARKS

In the Office Action mailed June 28, 2011, claims 1-4, 6-8 and 10-36 were pending and indicated as rejected. The Amendment meets one or more of the criteria set forth in Rule 116- does not introduce new matter, decreases the issue, and raises no issues which should require further search or consideration.

By this response, claim 1 has been amended to include the subject matter of claim 5 and claims 5 and 7 have been cancelled. Support for the amendment can be found in the original specification.

Reconsideration is respectfully requested in light of the forgoing amendments and remarks that follow.

Relative to the Examiner's comments regarding claim numbering. Applicants consulted PAIR. It appears that as of February 10, 2006 there were 38 claims. Some confusion appears to have settled in. Clarification is requested. It is clear from the rules that the PTO is ultimately responsible for the numbering of the claims.

The Examiner is thanked for the observation relative to claims 5 and 7. The amendment, upon entry, addresses the duplicate claim issue.

Claimed Invention

Applicants note in paragraph [0002] of the application, as filed, that it was known to employ spherical silica particles as carriers for feed stuff particles. Some disadvantages of these silica particles are mentioned in paragraph [0003] and include high water content, low purity and poor flow properties of loaded substances. Some problems are attributed to starting materials, considerable amounts of salts and expensive washing steps needed to remove the salts.

The present invention addresses these problems. The success of Applicants approach is established in the experimental section. Consider the Table on page 47 and paragraphs [0050] - [0053] and [0060] - [00061].[1] The proof of concept is established.

A source of granules suitable for use in the invention are identified as those associated with EP PS 0725037. See paragraphs [0008] and [0009].

Claim Rejections under 35 U.S.C. § 103(a)

I. Claims 1-2, 4, 6-8, 10-14, 20, 26-27 and 32-35 stand rejected as being unpatentable over Roman (US 6,171,602) in view of Deller et al. (US 5,776,240), Hasenzahl et al. (WO 03/037379) and the Degussa Press Release titled "Dry Binder – A New Concept for Pressed Powder." Applicants respectfully traverse.

Roman teaches a cosmetic composition which includes porous spherical silica materials. The Examiner recognizes a granular pyrogenic material like that claimed is not taught. Deller et al. is cited to show the existence of granular pyrogenic materials. (The Dellar et al. applications, taught and exemplified, are not used as a carrier in a cosmetic formulation.)

Hasenzahl et al. (WO 03/037379) teach the use of granular silica materials in pharmaceutical compositions to aid tableting (e.g. Tables 6 and 8). Flowability is mentioned in the Hasenzahl et al. examples.

[1] The results shown in the Table appearing on page 47 of the specification clearly establish the advantages for the claimed adsorbate. The form of silica, AEROPRIL®, employed by the invention is compared to precipitated silica-SIPERNAT® 22, SIPERNAT® 50, and Syloid 244 FP (Grace). The tests used for flow rating, slope angle and bulk density are recognized. It is clear from the Table that each of the variables measure show superiority for the claimed product over products which employ a different form of synthetic silica, precipitated silica. It is also clear from the Table that this superiority is more attributable to the form of the silica than to the active ingredient type. The comparative examples each employ Eucalyptus oil as does Example 4. Examples 1-3 are similar to the results shown in Example 4 than are the results reported for the comparative examples. Technical Bulletin No. 31 entitled "Synthetic Silica as a Flow Aid and Carrier Substance" is enclosed for completeness and consideration, especially of, sections 4.1-4.8, 6.1 and 9.

The Degussa Press Release teaches using AEROPERL to adsorb a liquid binder. When the AEROPERL/liquid binder mixture is pressed during the "tableting" process the oil binder is released.

The reason why the primary reference would have been modified to include the Deller et al granular silica product to attain the functions taught by the remaining secondary references is not entirely clear.

In any event, to the degree a prima facie case of obviousness is deemed to have been established; it is believed that the results shown relative to improved flowability would rebut the prima facie case. See footnote 1.

Reconsideration and withdrawal of the rejection are respectfully requested.

II. Claims 1, 3, 28 and 30-31 stand rejected under 35 U.S.C. § 103(a) as being unpatentable over Minemoto (JP 02049707) in view of Deller et al., Hasenzahl et al., and the Press Release. The rejection as to claims 1, 3, 28 and 30-31 is respectfully traversed.

Claim 1 has been amended to include the subject matter of claim 5(7), which the Examiner deemed to be free of the rejection.

Minemoto teaches a B cpd. insecticide absorbed on porous grains in an amount of 5 – 50% by weight. Materials for the grains are identified. The silica is one but is not identified as to its type. The characteristics of the porous grains, e.g. spherical, are identified.

Deller et al., Hasenzahl et al., and the Press Release are discussed above.

The reason why the primary reference would have been modified to include the Deller et al granular silica product to attain the functions taught by the remaining secondary references is not entirely clear.

In any event, to the degree a prima facie case of obviousness is deemed to have been established; it is believed that the results shown relative to improved flowability would rebut the prima facie case.

Reconsideration and withdrawal of the rejection are respectfully requested.

III. Claims 1, 19, 21, 29 and 34 stand rejected under 35 U.S.C. § 103(a) as being unpatentable over Park et al. (US 5,654,258) in view of Deller et al., Hasenzahl et al. and the Press Release. The rejection as to claims 1, 19, 21, 29 and 34 is traversed.

As noted above, the amendment to claim 1 adds the subject matter of claim 5 (7). Claim 5 (7) was found to be free of the teachings of the combined references.

Park et al. teach a solid, water dispersible, storage stable trifluralin formulation. The triflurin is supported inside porous, finely divided carrier particles. Suitable carrier particles are described as being silica particles having a surface area of 150 to 250 m^2/g and having an absorbed water content of 2 to 12%, preferably 3 to 6% before loading of the trifluralin. H151L257 is identified as the silica used in the examples. H151L257 is a synthetic precipitated silica of a surface area 190-210 sq. meters manufactured by PPG (Taiwan). H151L257 is not a pyrogenic silica nor is it like the claimed granular pyrogenic silica. Other silica types are mentioned in col.12. None are mentioned as being pyrogenic silica. All appear to be precipitated silicas.

Deller et al., Hasenzahl et al. and the Press Release are discussed above.

The reason why the primary reference would have been modified to include the Deller et al granular silica product to attain the functions taught by the remaining secondary references is not entirely clear.

In any event, to the degree a prima facie case of obviousness is deemed to have been established; it is believed that the results shown relative to improved flowability would rebut the prima facie case.

Reconsideration and withdrawal of the rejection are respectfully requested.

IV. Claims 1, 15-18, and 22-23 stand rejected under 35 U.S.C. § 103(a) as being unpatentable over Peterson et al. (US 6,004,584) in view of Deller et al. (US 5,776,240) and the Degussa press release titled "Dry Binder – A New Concept for Pressed Powders" (June 12, 2003). The rejection as to claims 1, 15-18 and 22-23 is respectfully traversed.

Again, as noted above, the amendment to claim 1 adds the subject matter of claim 5 (7), which claim 5 (7) was found to be free of the teachings of the combined references.

Peterson et al. teaches highly absorbent body powders. These powders do not appear to be feedstuffs, foodstuffs, or plant protection agents as required by the claims. There is clearly no indication of a composition containing a chemical intermediate as intermediate would be understood in the art.

Silicates including Aerosil® and Cab-OSil® here are mentioned in col. 3. as absorbents (the "active" ingredient). Powder carriers are mentioned starting in col. 3 at line 44. None of the powder carriers is identified as silica.

Deller et al. and the Press Release are discussed above.

The carriers of Peterson et al. appear to be carbohydrates. Significant changes would need to be made to the Peterson et al. composition in order for it to resemble one that meets the description required by the claims.

V. Claims 1 and 24 stand rejected under 35 U.S.C. § 103(a) as being unpatentable over Technical Bulletin Pigments No. 31 (Degussa AG, November 1995) in view of Deller et al., Hasenzahl et al. and the Press Release. The rejection as to claims 1 and 24 is traversed.

The Technical Bulletin has been characterized by the Examiner as suggesting a silanized silica useful as an adsorbate for molasses in order to make a free-flowing binder.

Deller et al., Hasenzahl et al. and the press release are discussed above.

The reason why the primary reference would have been modified to include the Deller et al granular silica product to attain the functions taught by the remaining secondary references is not entirely clear.

In any event, to the degree a prima facie case of obviousness is deemed to have been established; it is believed that the results shown relative to improved flowability would rebut the prima facie case.

Reconsideration and withdrawal of the rejection are respect fully requested.

CONCLUSION

All of the stated grounds of rejections have been properly traversed, accommodated, or rendered moot. Therefore it is respectfully requested that the Examiner reconsider all presently outstanding rejections and that they be withdrawn. It is believed that a full and complete response has been made to the outstanding Office Action and, as such, the present application is in condition for all allowance.

It is not believed that extensions of time are required, beyond those that may otherwise be provided for in accompanying documents. However, in the event that additional extensions of time are necessary to prevent abandonment of this application, then such extensions of time are hereby petitioned under 37 C.F.R. 1.136(a), and any fees required therefore are hereby authorized to be charged to Deposit Account No. 02-4300, Attorney Docket No. 032301.440.

Respectfully submitted,

SMITH, GAMBRELL & RUSSELL, LLP

By: ______________________

Thomas G. Wiseman, Reg. No. 35,046
1130 Connecticut Avenue, Ste. 1130
Washington D.C. 20036
Telephone: 202.263.4300
Facsimile: 202.263.4320

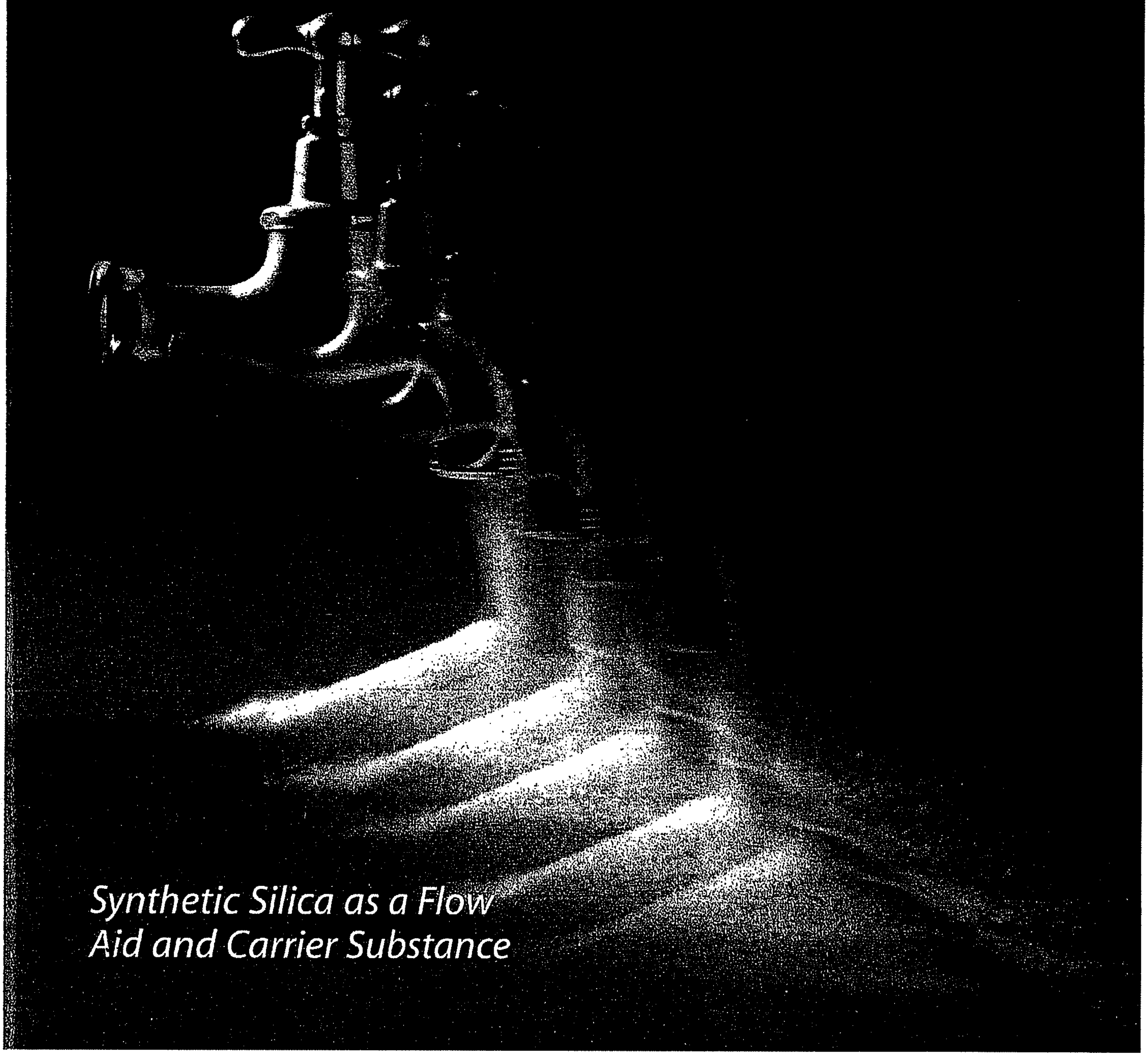
Dated: September 7, 2011

degussa.

creating essentials

Technical Bulletin Fine Particles

Number 31



Synthetic Silica as a Flow Aid and Carrier Substance

Synthetic Silica as a Flow Aid and Carrier Substance

Synthetic silica have gained importance in numerous fields of application throughout the world since the Second World War. These new markets include the use of synthetic silica as flow aid and as carrier substance for widely varying fields of application.

In the course of constantly advancing development, Degussa AG has introduced new products into the market during recent years with specific characteristics for special applications. This publication summarizes the types recommended by Degussa AG, and points out special possibilities for their application.

Dr. Horst Ferch *Rolf Oelmüller* *Brigitte Grinschgl*

Applied Technology Silica & Pigments
Degussa AG

Our cover shows:
Symbolic demonstration of the flow behaviour

Table of Contents

1. *Introduction*

Synthetic silica have found their way into a wide variety of applications in numerous branches of industry. This applies above all in those cases where the synthetic silica are not used as raw materials, but as additives. When added in small amounts, they often serve as „problem solvers". As raw materials, synthetic silica are used in the rubber industry, in plant protection and feedstuffs they are used as excellent carriers.

The large number of other applications in different fields of use is summarized in this publication. Simultaneously, special products with new characteristics will be introduced and described comparatively in detail. This information is intended to widen the use of materials in powder form and to improve the characteristics of these materials.

Substances in powder form tend to form agglomerates and to cake together regardless of the composition and use. As a consequence, the packaging, storage, and above all the handling of these materials is made difficult.

The increasing rationalisation and automation in industry, however, demands a good flow behaviour of the materials in powder form, as well as high stability during storage, and when subjected to weathering and pressure loading.

The characteristics of powders depend namely on the particle size in different ways. **Figure 1** first shows the dependence of the homogeneity or uniformity on the particle size. This property decreases in a characteristic way with an increasing particle size. In other words, this means that small particles must naturally be very uniform, see [1].

Figure 1 additionally shows the dependence of the ratio of adhesion force per mass on the particle size. In the case of small particles, the ratio of adhesion force per mass is extremely high. **Figure 2**, in a similar way shows the dependence of the flowability of a bulk material on the particle size. This property is excellent from a mean particle size of about 0.3 mm = 300 µm upward.

In this publication, the terms „flow aid" and „agent to improve the flowability" are used synonymously. In principle, the expression „anticaking agent" does express an only slightly different subject.

Figure 1: *Qualitative dependence of the homogeneity and of the ratio of adhesion force / mass of particles as a function of the particle diameter according to [2]*

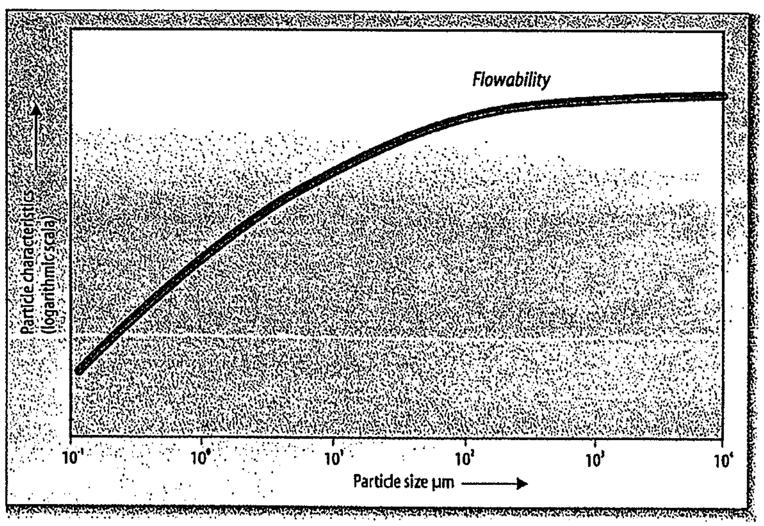


Figure 2: *Qualitative dependence of the flow behaviour of a bulk material on the mean particle size according to [2]*

2. *Finely Divided Degussa Products to Improve the Flow Behaviour of Materials in Powder Form and as Carrier for Liquid Active Substances*

Degussa AG produces synthetic silica according to various processes in twelve plants on three continents. Details of the production and process-related differences are discussed in detail in No. 32 in this series of Technical Bulletin Pigments. On the following pages, the products of interest for improving the flow behaviour will be presented, and at the same time their application as carriers for liquids will be discussed. All Degussa products mentioned in this publication are formed by finely divided primary particles which then become aggregated or agglomerated, see [3].

2.1 Precipitated Silica

Precipitated silica are produced from a water glass solution to which sulphuric acid is added under certain conditions. Therefore, they develop in the aqueous phase. Depending on the precipitation conditions, products can be derived with smaller or somewhat larger primary particles which essentially determine the size of the specific surface.
The precipitates produced in this way are washed out and dried according to various methods, see **Figures 3** and **4**. All precipitated silica have a drying loss of about 6 % by weight and also an ignition loss in the same order of magnitude.

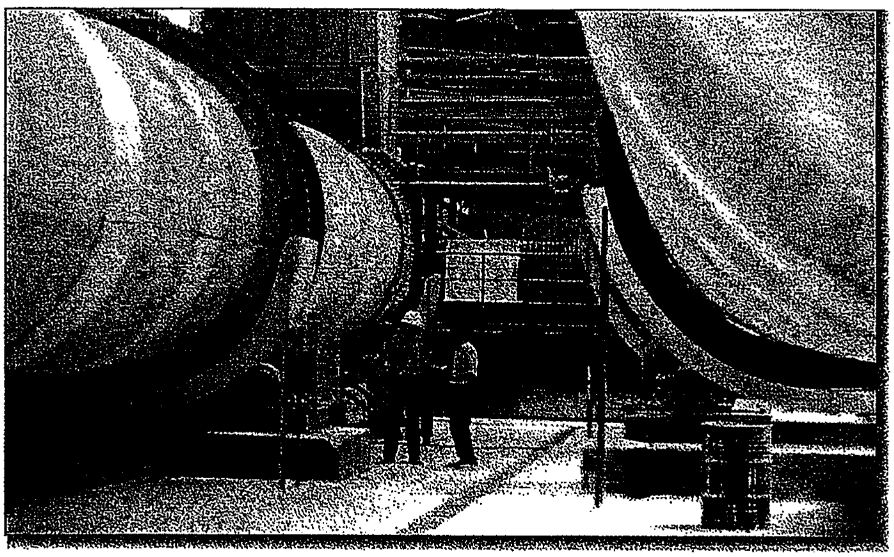


Figure 3: *Partial view of rotary driers for the production of precipitated silica*

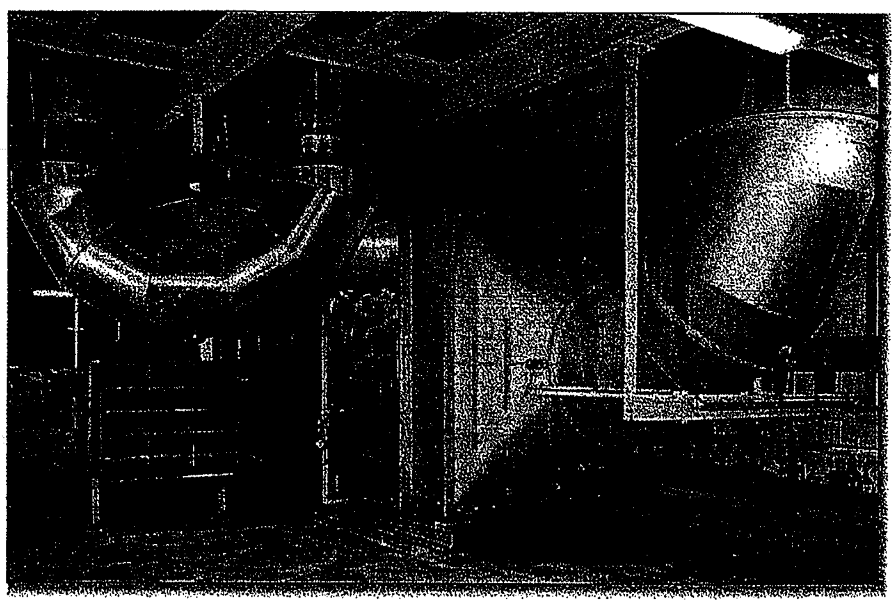


Figure 4: *Partial view of spray drier for the production of precipitated silica*

2.1.1 Spray Drying of Precipitated Silica

If the drying process is carried out by spray drying, almost spherical particles are formed with a size of about 50 µm to 320 µm which by themselves have excellent flow properties. These particles are largely porous. For this reason, spray dried precipitated silica have a very good adsorptive capacity for liquids. With the aid of such silica, liquids or semisolid masses can be converted into free flowing powders. The silica content in this type of concentrate usually ranges between 28 % and 35 %. As a rule, unground, spray dried, precipitated silica serve as excellent carriers, but are used for free flow in only a few cases.

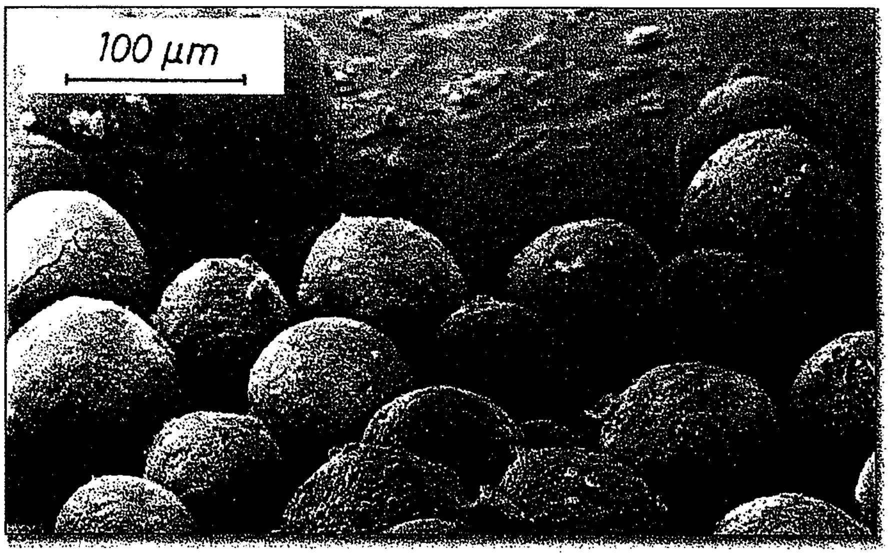


Figure 5: *SEM of SIPERNAT® 22*

Figure 6: *SEM of SIPERNAT® 22 S*

It is possible to grind spray dried precipitated silica. For grinding, various mills are used which permit a controlled adjustment for the fineness. As a result, above all the tamped density and the particle size change, as the following examples show:

SIPERNAT® 22	280 g/l	~ 100 µm
SIPERNAT® 22 S	90 g/l	~ 7 µm
or		
SIPERNAT® 50	180 g/l	~ 50 µm
SIPERNAT® 50 S	90 g/l	~ 7.5 µm
SIPERNAT® 500 LS	75 g/l	~ 4.5 µm

SIPERNAT® 22 S, SIPERNAT® 50 S, and SIPERNAT® 500 LS are typical flow aids, i.e. they are used to improve the flow behaviour of other materials. The additional designation „S" indicates a fine grinding, while „LS" indicates even more finely ground, special products. **Figure 5** shows a scanning electron micrograph (SEM) of SIPERNAT® 22; for comparison purposes, **Figure 6** reproduces a corresponding micrograph of SIPERNAT® 22 S.

2.1.2 Conventional Drying of Precipitated Silica

During the drying in a conventional way, for example in rotary driers, the time for drying is considerably longer. In every case, a grinding must follow the conventional drying. SIPERNAT® 320 and SIPERNAT® 320 DS are produced in this way. Similar to the supplementary designation „LS", the supplementary designation „DS" indicates a more intensive grinding. The flow properties of these products are distinctly lower than those of the unground spray dried ones. Mean particle size and tamped density again depend on the degree of grinding, for example

SIPERNAT® 320	220 g/l	~ 15 µm
SIPERNAT® 320 DS	75 g/l	~ 5 µm

2.1.3 Grinding

Whilst particle size is greatly reduced, it is remarkable that the size of the specific surface is not influenced by the grinding.

2.2 Hydrophilic AEROSIL®

The various types of AEROSIL® are produced according to the process of high-temperature flame hydrolysis during which silicon tetrachloride is hydrolyzed in an oxyhydrogen gas flame. Details of this process are described in Edition No. 11 in this series of Technical Bulletin Pigments.

In contrast to the precipitated silica, therefore, the types of AEROSIL® are not derived from the aqueous phase, and they are also not ground. The tamped density of the AEROSIL® types lies at about 50 g/l. The size of the specific surface is used to classify the different grades.

For example, the most important product, AEROSIL® 200, has a specific surface of 200 m²/g. The same statement applies for AEROSIL® 380, with a specific surface of 380 m²/g.
Figure 7 shows a transmission electron micrograph (TEM) of AEROSIL® 200 which makes it possible to recognize the tiny primary particles.

When the AEROSIL® grades leave the production plant they have a drying loss of less than 1.5 % by wt. and an ignition loss of 1 % by wt.

2.3 Hydrophobic Silica

Both, precipitated silica and the AEROSIL® types can be after-treated in a second production step to render the naturally imparted hydrophilic surface of the silica hydrophobic. This is accomplished by chemically reacting suitable chlorosilanes with the silanol groups on the silica surface. Then the silica are no longer wetted by water. Corresponding products are e. g. AEROSIL® R 972 and AEROSIL® R 812 as well as SIPERNAT® D 10, SIPERNAT® D 17, SIPERNAT® C 600, and SIPERNAT® C 630.

These hydrophobic silica differ in terms of the type of the reaction agent; for example, all products with the exception of AEROSIL® R 812 have dimethylsilyl groups. In contrast, AEROSIL® R 812 is a trimethylsilyl derivative. These special silica are good processing aids to improve the flowability of formulations.

For this purpose, amounts of 0.1 to 0.3 % added are generally adequate. Due to the hydrophobic behaviour, these specialty silica adsorb practically no water even at high atmospheric humidities.

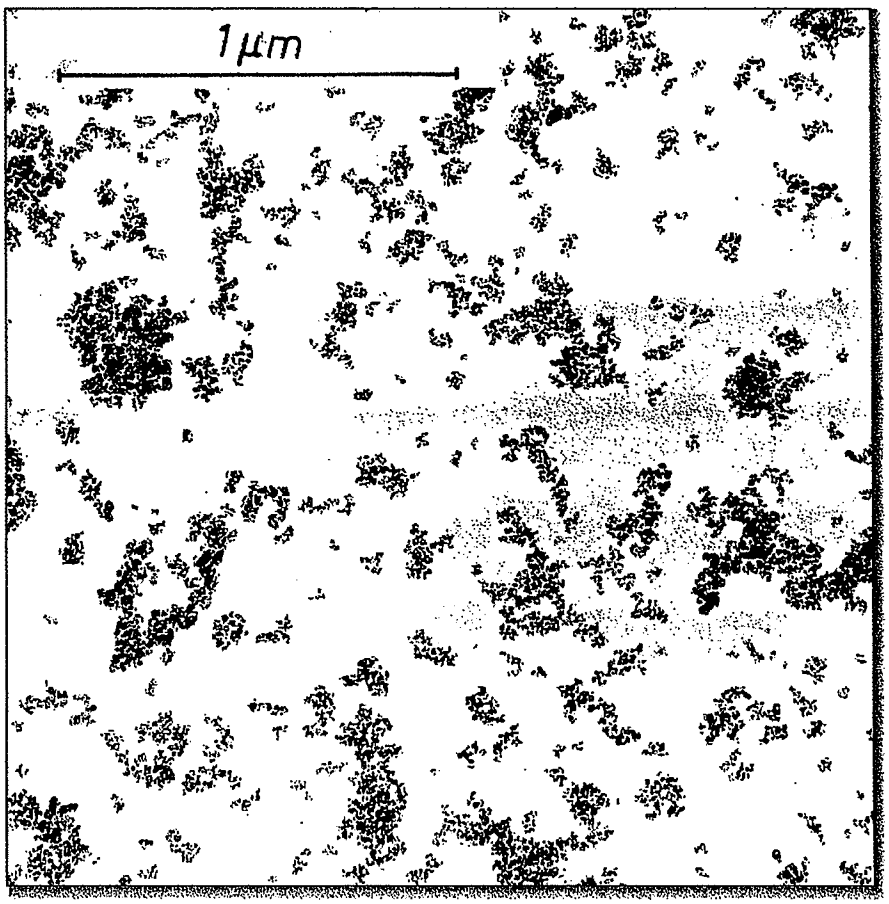


Figure 7: *Transmission electron micrograph (TEM) of AEROSIL® 200*

Figures 8 and **9** show the amounts of water vapour adsorbed by small samples of AEROSIL® R 812 as well as by SIPERNAT® D 17. In both cases, the particular base product, which served for production of the hydrophobic variant, is also shown for comparison purposes.

Figure 8: *Water vapour absorption isotherms at room temperature of AEROSIL® 300 (hydrophilic base material) and AEROSIL® R 812, measured on small samples*

Figure 9: *Water vapour absorption isotherms at room temperature of SIPERNAT® D 17 and of the hydrophilic base silica ULTRASIL® VN 2, measured on small samples.*

Figure 10 clearly illustrates the concept of „hydrophobicity". In this picture, drops of water lie on moulded tablets, which were pressed from hydrophilic and hydrophobic silica. On the hydrophilic silica the drop of water lies flat, the „contact angle" is less than 90°.

In contrast, on the surface of the hydrophobic silica the spherical form of the water drop can clearly be seen, the contact angle is greater than 90°; also see No. 42 in this series of Technical Bulletin Pigments.

2.4 AEROXIDE® Alu C

AEROXIDE® Alu C is produced from aluminium trichloride according to the AEROSIL® process. Even though the average primary particle size of this product very closely approaches that of AEROSIL® 200, the specific surface is only about 100 m²/g because of the higher density of the Al_2O_3 – it lies at about 3.2 g/cm³. The tamped density, 80 g/l, is higher than in the case of AEROSIL® 200.

In contrast to synthetic silica, AEROXIDE® Alu C always becomes positively charged, see 3.7 on this point.

SIPERNAT® D 17 *SIPERNAT® 320*

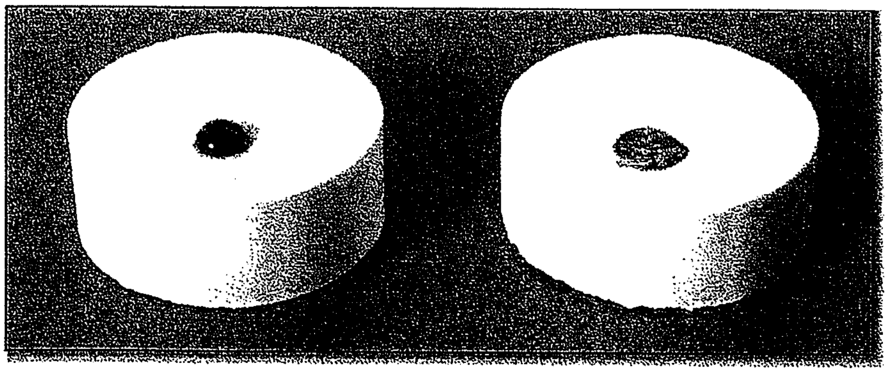


Figure 10: *Demonstration of the wetting of a hydrophobic and a hydrophilic silica*
Left: SIPERNAT® D 17
Right: SIPERNAT® 320

3. *Comparison of the Characteristics of Degussa Precipitated Silica*

In addition to the general data relating to the properties of Degussa silica, this section presents and compares the most important characteristics for applications involving their use as flow aids and carrier substances. Further physico-chemical data are given in the overview tables at the end of this publication. For purposes of completeness, AEROXIDE® Alu C is also included in this comparison.

3.1 Tamped Density and Tamped Volume

In **Figure 11**, the tamped densities according to ISO 787-11 of the silica considered here are compared.

This comparison differentiates between three groups: heavy, medium heavy, and light silica. Even though this classification appears somewhat arbitrary, the representation nevertheless gives an overview of the tamped densities of the Degussa silica. The chemical aftertreatment has no influence on the tamped density. Tamped densities give an indication of the silo size or space requirements for storage. Further general questions relating to the handling can also be anticipated from these densities, for example what type of conveying system is suitable. Edition No. 28 in this series of Technical Bulletin Pigments describes the handling of synthetic silica in detail. Questions of conveyance are part of this handling. **Figure 12** shows the corresponding tamped volumes.

Figure 11: *Comparison of the tamped densities of Degussa silica*

Figure 12: *Comparison of the tamped volumens of the Degussa silica shown in Figure 11*

3.2 Agglomerate Particle Size

Figure 13 gives a comparison of the agglomerate particle sizes present in the Degussa silica. This characteristic is of great practical importance, because very finely divided silica are especially good flow aids. Namely, the finer a silica is, the more particles are available for coating other particles when a given amount of silica is added. It is not possible to give the agglomerate particle size for the AEROSIL® grades or for AEROXIDE® Alu C because this parameter depends on the particular dispersion conditions.

3.3 Dibutyl Phthalate Absorption

The dibutyl phthalate method according to DIN 53 601 determines the void volume in a given solid under standardized conditions with the aid of dibutyl phthalate as measuring liquid, see Figure 14. A higher test value corresponds to a higher void volume. The result of the test is given in g liquid per 100 g substance. In general, the DBP absorption, as this method is named for short, characterizes the absorptive capacity of a substance.

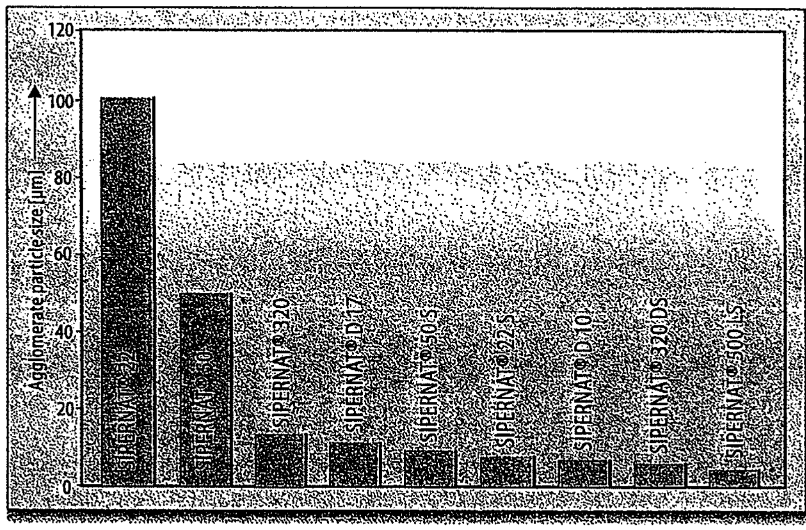


Figure 13: *Comparison of the agglomerate particle sizes of Degussa silica. SIPERNAT® 22 and SIPERNAT® 50 were studied by sieve analysis, the other types with the Coulter Counter. For the majority of all products, the 100 µm capillary was used, however the 50 µm capillary was used for LS and DS products*

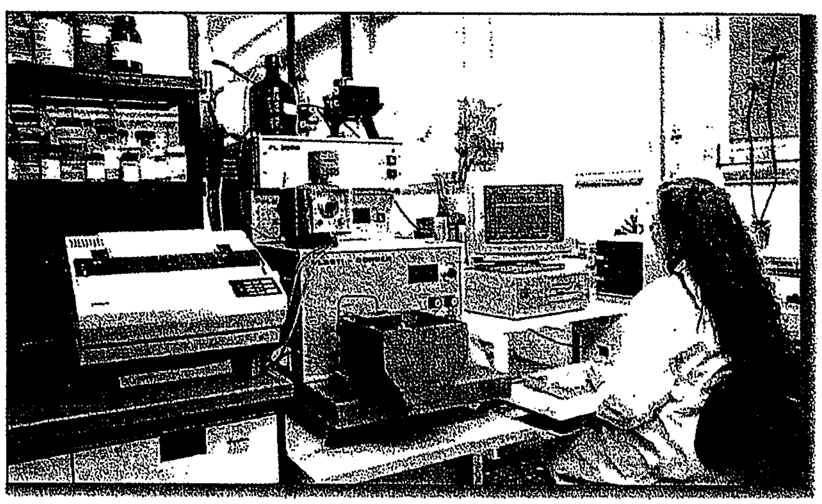


Figure 14: *Plasti-Corder PLE 331 with attachment „PL 2000" to determine the DBP Number Manufacturer: BRABENDER OHG, Kulturstr. 51, D-47055 Duisburg*

This absorptivity is of special importance for the conversion of liquid or paste-like materials into powder form. The higher the DBP absorption, the less silica is required to produce a powder with good flow properties.

In **Figure 15** the DBP absorption values of selected Degussa silica are compared. The types based on SIPERNAT® 50 and AEROSIL® 380 have the highest absorptive capacity. This group with values greater than 300/100 g is followed by another group with values of 270 to 225 g/100 g.

3.4 pH Value

In **Figure 16** the pH values are compared for all silica discussed here. The pH value is often of importance when a reaction can take place with the material to be treated. It can be recognized from **Figure 16** that the majority of Degussa silica, for example all hydrophilic SIPERNAT® types have pH values lying near the neutral point. All hydrophilic AEROSIL® types and AEROSIL® R 972 lie in the more acidic range, while AEROSIL® R 812 can exceed the neutral point because of its special aftertreatment. A true exception is found in the case of SIPERNAT® D 10 which represents an „alkaline reacting silica".

Figure 15: *DBP absorption of Degussa silica*

Figure 16: *pH values of Degussa silica*

All pH values were measured according to ISO 787-9 at 4 % or 5 % in water or in a water-methanol mixture. The samples were not pretreated. In the case of hydrophobic products the chemical aftertreatment has an effect on the pH value, however, the degree of grinding has no influence.

3.5 Other Characteristics

The **chemical composition** respectively the impurities contained play practically no role in improving the flowability. In some cases this statement also applies for the adsorbency.

In contrast, the statement that all Degussa silica and also AEROXIDE® Alu C cause no abrasion is of utmost importance. Abrasion can disrupt the operation of conveying equipment or processing machines, and under certain conditions can also contaminate a material.

It has already been mentioned in Section 2 that all silica treated in this publication, and AEROXIDE® Alu C as well, are built up of very finely divided primary particles. Therefore, it is not surprising that the **specific surface** of the Degussa products described here is very large. In all cases it is larger than 100 m^2/g. Consequently, the Degussa products considered here differ distinctly from natural products. As a rule, natural products, even when they have been ground well, attain only a few m^2/g. As a result, natural products can also not induce the improvements which are possible with synthetic products.

Due to high specific surfaces, Degussa silica show a tendency to adsorb water vapour from the air under humid conditions, see **Figures 8** and **9** on this point. As a result of the chemical aftertreatment, this can largely be avoided. The Degussa precipitated silica are set to a drying loss of 6 % by wt. during the drying process. On the other hand it should be stated that adsorbed water is being released under dry conditions.

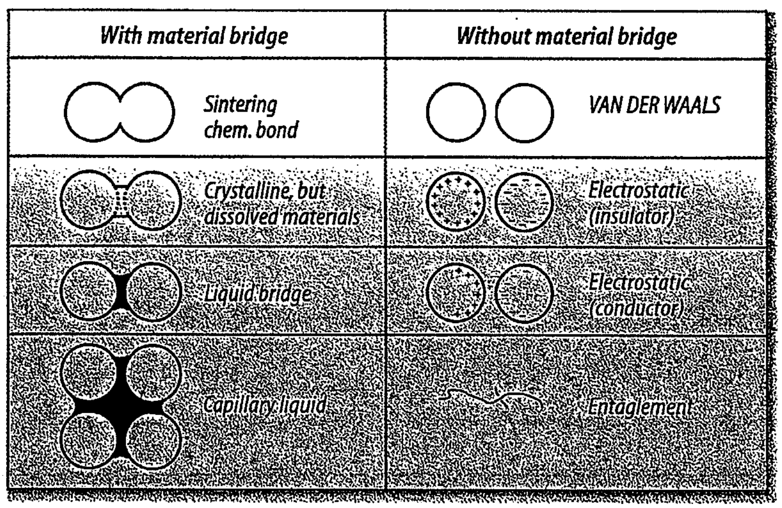


Figure 17: *Schematic representation of important bonding mechanisms which results in agglomeration [7]*

4. *Fundamentals of the Flow Behaviour of Powders and of the Functioning of Flow Aids*

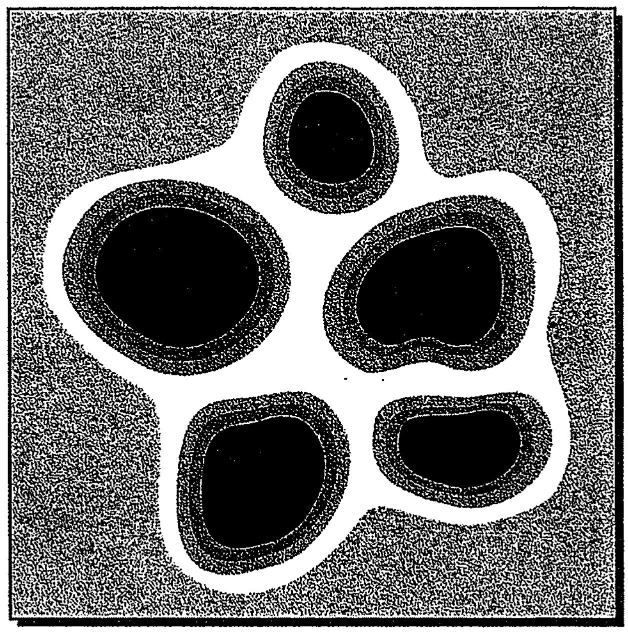
4.1 General

The flowability of powders is determined essentially by the characteristics of the powder in question. The particle adhesion between solid matter particles in a gaseous atmosphere was only studied systematically after the Second World War, for example (4 -7).
An overview of the bonding mechanisms important for the agglomeration is given in **Figure 17.** As generic criterion for the division of the bonding mechanisms, SCHUBERT selected those with and others without material bridges [7].

These mechanisms can be either solid bodies of the same material (for example sintered bridges, chemical bonds, crystallization and structural changes) or liquid bridges, as well as adhesion due to the capillary liquids in the partially or completely filled pore space.

4.2 Adhesion Due to Sintering

Materials with a low melting point, for example fats or waxes, develop a soft surface at rising temperatures such as repre-



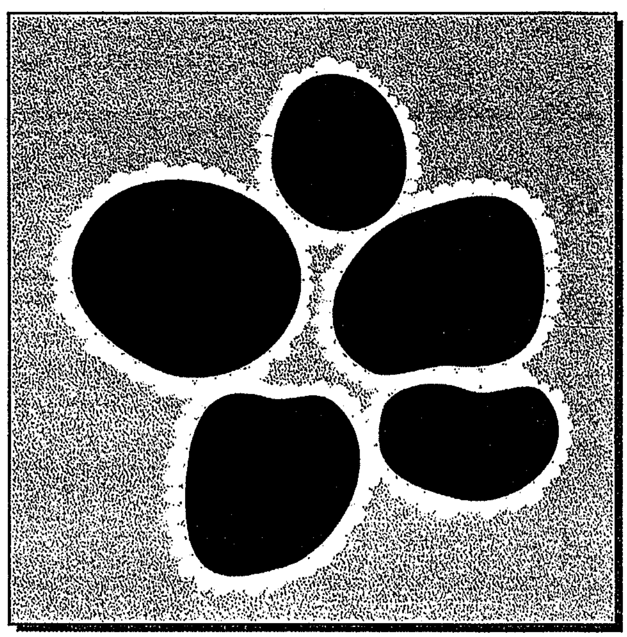


Figure 18 *to* **20** *show clearly how low melting points result in the particles sticking together and how finely divided, highly absorbent silica coat the particles absorbing the liquid and consequently prevent caking*

sented, for example, in **Figure 18**. The result of this is that the individual particles stick together. This condition is shown by **Figure 19**. As an estimate, it is assumed today that at least 60 % of the absolute melting temperature must be reached before sintering processes occur [7]. Through the addition of suitable synthetic silica in the amount of 0.2 to 2 %, for example the highly absorbent, finely divided silica SIPERNAT® 22 S or SIPERNAT® 50 S, the individual particles can be coated and separated from each other. **Figure 20** shows this condition. In this way a caking of the particles is effectively prevented. In the field of Galenics, primarily AEROSIL® 200 is used to prevent sintering processes in pharmaceutical active substances [8, 9].

4.3 Adhesion Due to Crystallization and Structural Changes

Solid matter bridges between particles can develop due to recrystallization and structural changes [7].

The addition of absorbent, finely divided, synthetic silica to such a mixture prevents caking by

- removal of the liquid film by absorption,
- coating and therefore separation.

In order to prevent these undesired effects, 0.2 to 2 % of SIPERNAT® 22 S or SIPERNAT® 50 S are generally recommended. During the tabletting of pharmaceutical compounds, such structural changes occur fairly often because of high moulding pressures. In these cases, amounts of 0.05 to 0.5 % of AEROSIL® 200 are adequate, see **Table 1** on this point.

Material	Mean particle diameter µm	Optimum addition %	Volume decrease %
Corn starch	13.2	0.5	34.1
Lactose	140	0.05	23.9
$MgCO_3$	65.5	0.05	7.2
TiO_2	3.6	1.00	12.5
ZnO	11.2	0.25	7.5
MgO	62.8	0.05	4.1
Lactose granules	300	0.05	9.2

Table 1: *Optimum amounts of AEROSIL® 200 added to various tabletting aids according to TAWASHI [10]*

4.4 Inadequate Flowability Due to Wide Particle Size Distribution or Uneven Particle Shape

If a substance consists of particles of different sizes, cases of separation can easily occur because during transfer of the substance from one vessel to another or during transportation the larger particles move faster than the small ones. Additions of 0.2 to 1 % of the finely ground SIPERNAT® 320 DS or SIPERNAT® 22 S coat the particles, and a ball-bearing effect is achieved. In addition, a certain standardization of the particle size is caused. A separation must no longer be feared.

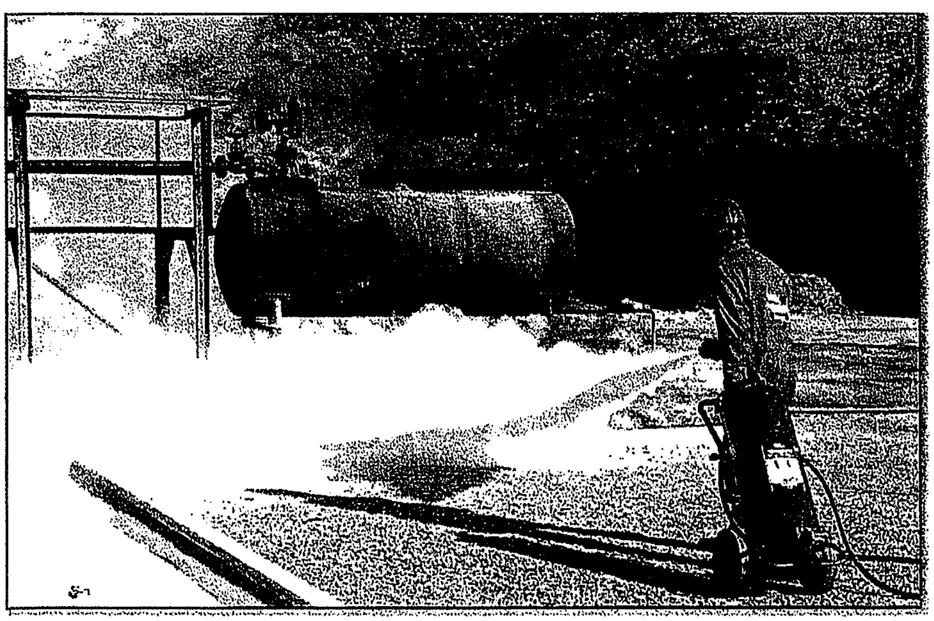


Figure 21: *Outstanding flowability is a basic requirement for the effective functioning of powder-type fire extinguishers*

For the flowability of materials, the shape of the particles composing this material likewise plays a considerable role. An uneven surface can have the result that

– increased friction occurs, and
– the particles become „hooked" together.

Figure 22 shows such a situation schematically. In this case also, 0.2 to 1 % of the finely ground SIPERNAT® 320 DS or SIPERNAT® 22 S is adequate to induce the ball-bearing effect and in this way develop good flowability.

Figure 22 *to* **24** *demonstrate how uneven particles shapes result in poor flow behaviour due to increased friction, and how finely divided silica induce better sliding and thus lead to improved flow behaviour*

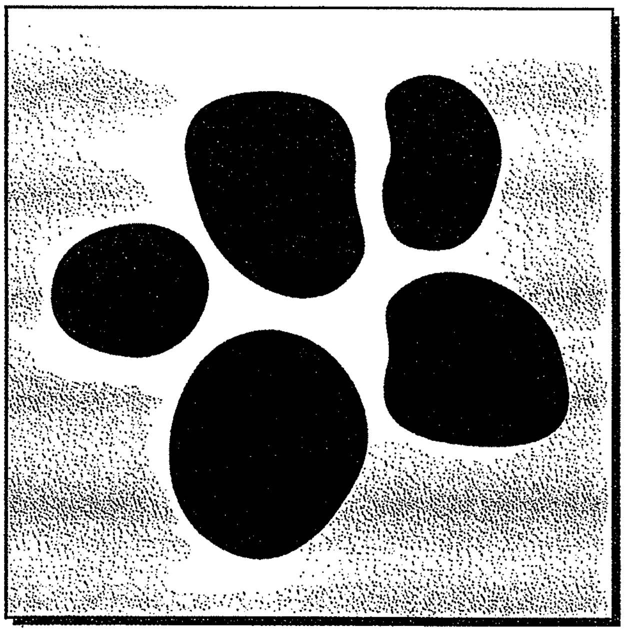
Figures 23 and **24** show this condition. When these figures are compared, it can be recognized that the volume of the mixture in **Figure 22** has become smaller because the particles are now packed more densely. **Table 1** presents data on how great this compacting effect is in the case of tabletting aids. Similar effects are also to be found with other classes of materials.

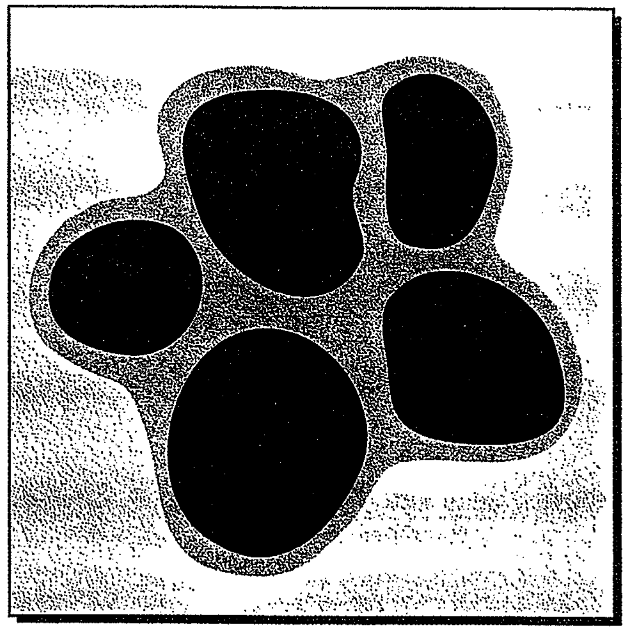
The significance of the surface roughness for the various adhesion mechanisms was studied in 1974 [11]. With an increasing degree of roughness, the effective spacing increases, and as a result the adhesion capacity decreases [7].

4.5 Adhesion Due to Liquid Bridges

Many materials form a film of liquid, e.g. water or oil, on the surface. During storage, the individual particles are in close contact. The surface tension of the liquid holds these particles together.

If the material is water-soluble, fluctuating atmospheric humidity can cause recrystallization and bridge formation, such as is described in 4.3. Additions of 0.2 to 2% SIPERNAT® 22 S or SIPERNAT® 50 S have the effect that the liquid film is removed by absorption and as a result the particles are completely coated by the silica. Consequently, they are separated spacially from each other. **Figures 25 to 27** show these processes in a schematic representation.





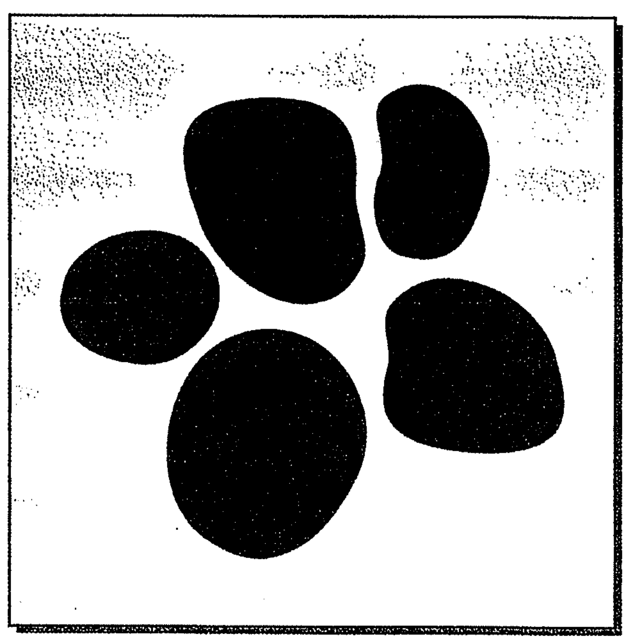


Figure 25 *to 27 show schematically how the surface tension of the liquid film holds the particles together, and how finely ground, absorbent silica establish the good flowability again by removing the liquid by absorption and by the spacing effect*

If the liquid film is water, e.g. the material is hygroscopic, the use of hydrophobic silica is recommended. Additions of 0.05 to 0.3 % AEROSIL® R 972 or SIPERNAT® D 17 become deposited on the water film, resulting in a separation of the particles. The processes that take place here are shown by **Figures 28 to 30.**

Due to liquid bridges, the adhesion forces can be calculated according to SCHUBERT for all rotation-symmetrical bridges [12]. Since corresponding results of adhesion force calculations cannot be given in closed form, a representation in graphs is expendient [7]. The adhesion forces generally increase with increasing atmospheric humidity, whereby the dependency only prevails starting at a medium ambient moisture [13].

Figure 28 *to* **30** *in contrast to Figures 25 to 27, show how hydrophobic silica float on the water film and consequently prevent the individual particles from touching each other*

4.6 VAN DER WAALS Adhesion Forces

In the case of materials in powder form, VAN DER WAALS forces develop due to interaction of the dipole moments of molecules. They are always present. For some model bodies they can be calculated [14]. A frequently used mean value for VAN DER WAALS adhesion forces lies at $8 \cdot 10^{-19}$ J. For the greater adhesion forces in the case of particles touching each other, a contact spacing of 0.4 nm is used in calculations [11].

4.7 Electrostatic Attraction

With regard to non-conducting powders, an excess charge is often observed which in the case of antipole charging results in forces of attraction. During the conveying of powders through pipes, or during mixing, sieving, and grinding processes, this electrostatic charge always develops.
The maximum value of the excess charge is 100 e/µm^2 ($e = 1.6 \cdot 10^{-19}$ A s) [14].

In many cases, experiments with AEROSIL® 200 or SIPERNAT® 22 S are successful in such a way that the electrostatic charging is reduced. Since many powders become charged negatively, the highly-dispersed AEROXIDE® Alu C, when added in small amounts, is often capable of compensating for the charging [15, 16]. For this purpose, added amounts of 0.05 to 0.3 % are adequate to ensure processing operations with no problems. Table 2 shows some examples where finely divided materials are used to reduce the electrostatic charge.

4.8 Comparison of the Various Adhesion Forces with Each Other

According to SCHUBERT, the adhesion forces can be calculated for some adhesion mechanisms for completely smooth, non-deformable, solid bodies [7]. For this purpose, it was necessary to assume the maximum surface charge was 100 e/µm^2 in the case of the model of the electrical insulator, and to assume a complete wetting (boundary angle equal to 0) for the model of the liquid bridge. Accordingly, in the case of the sphere/plate system, and a contact distance of $4 \cdot 10^{-4}$ µm, with a given sphere diameter the adhesion force increases in the following sequence:

- particle adhesion
- electrostatic adhesion
- VAN DER WAALS adhesion forces
- liquid bridges.

At a sphere diameter of 0.1 µm, the first two adhesion forces mentioned are less than 10^{-5} dyne, the VAN DER forces are about 10^{-3} dyne, and in the case of the liquid bridges they are about $5 \cdot 10^{-2}$ dyne.

Material tested	Field of use	Additive
1 Sulphur	Pesticides (viticulture)	0.3 % AEROSIL® 200
2 PVC powder	Thermopl. shaping	0.5 % AEROSIL® R 972
3 S-PVC powder	Thermopl. shaping	0.3 % AEROXIDE® Alu C
4 Proxyphyllin	Pharmacy	0.45 % AEROSIL® 200
5 Whirl sintering powder	Coating	0.2 % AEROSIL® R 972 + 0.2 % AEROXIDE® Alu C
6 Anhydrous citric acid	Pharmacy	1.0 % AEROSIL® 200
7 Carbowax 6000	Gen. chem. industry	1.0 % AEROSIL® 200
8 Polyethylene powder	Rotary centrifugal casting	0.3 % AEROXIDE® Alu C
9 Cellulose powder	Pharmacy	0.6 % AEROSIL® 200
10 Polymers	Packaging	AEROSIL® 200
11 Sheets of paper	Paper industry	AEROXIDE® Alu C
12 Pastic sheeting	Packaging	AEROSIL® 200
13 Aspirin	Pharmacy	up to 0.4 % AEROSIL® 200
14 Aspirin	Pharmacy	up to 0.7 % AEROXIDE® Alu C
15 Silver halides	Photogr. film production	AEROSIL® 200
16 General	Test sifting	up to 0.3 % AEROXIDE® Alu C

Table 2: *Compilation of some known applications of highly-dispersed materials as aids to reduce electrostatic charging according to [16]*

5. *Measurement Techniques*

5.1 Scientific Methods

In many cases, the occurrence of flow problems in daily practice depends on the type of flow profile in a silo [17, 18]. The flow profile defines the way in which the bulk material flows in the silo. Here, a differentiation is made between „mass flow" and the undesired „core flow", see **Figure 31** on this point. In the case of mass flow, the entire contents of the silo is set in motion as soon as bulk material is withdrawn. There are no „dead zones" here, and the bulk material flows along the wall of the hopper.

In contrast, during core flow, bulk material only flows out from a central zone. A discharge funnel develops, and dead zones form on its periphery.

In addition to the bridging described under 4, the undesired „shaft formation" can also occur during core flow. In this case, bulk material flows out from only a central pipe, so a complete emptying of the silo is not possible.

Whether mass flow or core flow takes place in a silo depends on [19].

- the slope of the hopper wall, measured with respect to the vertical,
- the shape of the hopper (conical or rectangular),
- the wall friction angle between the bulk material and the wall material, and
- the effective angle of friction.

The angles of friction can be measured with shear instruments or powder rheometers.
The following serve for this purpose:

- the translation shear instrument according to JENIKE [17, 19, 20],
- the ring shear instrument according to SCHUBERT [21, 22].

The JENIKE instrument is in relatively widespread use despite certain disadvantages which, for example, are described in [2]. However, neither instrument is suited to carrying out series of experiments, such as those required to improve the flowability through the use of synthetic silica as additives, because they both involve considerable time and expenses. Shear instruments are used when expedient silo installations, and especially optimum discharge equipment, are to be built.

Figure 31: *Representation of mass and core flow. For details see DIN 1055, Sheet 6*

5.2 Methods for Daily Practice

5.2.1 Flowability by Funnels

In order to determine the flowability without a pressure treatment, KLEIN suggested back in 1968 (6) the use of siliconized glass funnels with different orifice diameters. Such a series of measuring vessels is shown in **Figure 32**.

Funnel No. Evaluation No.	Orifice diameter mm	Evaluation during smooth flow through funnel orifice
1	2.5	very good
2	5	↑
3	8	
4	12	
5	18	
6	24	
7		unsatisfactory (does not run through No. 6)

Table 3: *Table for evaluation of the flowability according to [23] with glass funnels. These funnels are 80 mm high, with an inside diameter of 38 mm*

The evaluation is made with the Grades 1 = very good flow behaviour, i.e. the powder to be studied flows out from funnel No. 1 with the smallest opening without stopping, to Grade 7 = unsatisfactory flow behaviour, i.e. the powder no longer flows even through funnel No. 6 with the largest orifice. **Table 3** clearly shows the orifice diameters and evaluation criteria.

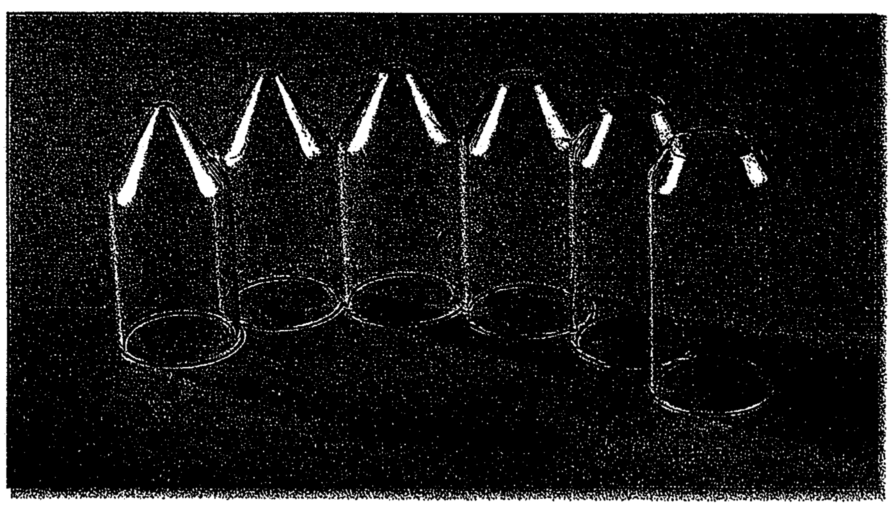


Figure 32: *Set of glass funnels*

The procedure needs always to be done under the same conditions, e.g. sequence of funnels. The result of the test is given by the number of the funnel through which the powder still flows without stopping or clogging, see **Figure 33**.

5.2.2 Flowability by Cone Height

During the measurement of the flowability by the cone height of a powder, the following steps are taken:

A metal sieve is fastened at a distance of 30 - 100 mm over a solid metal cylinder with a diameter of 50 mm and a height of about 80 mm. The distance between the metal sieve and the metal cylinder depends on the flowability of the powder to be measured, and should be somewhat greater than the cone height of the powder in the particular experimental series with the poorest flow characteristics and fixed at this height. The powder is poured onto the sieve, and is passed gently through the sieve by hand with the aid of a spatula, see **Figure 34**.

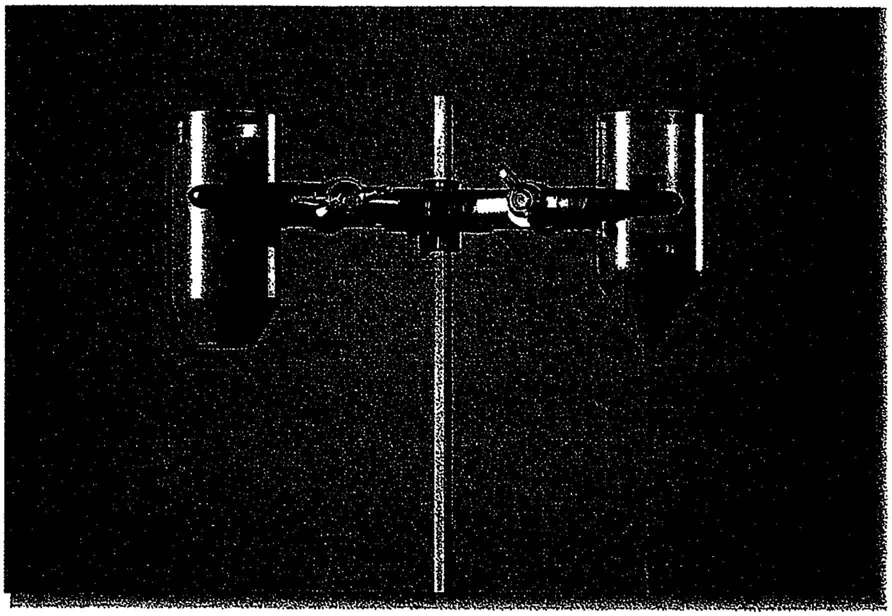


Figure 33: *Example of the flow from a glass funnel*

The powder falling down onto the metal cylinder builds up to form a cone. Powder is passed through the sieve until a geometrically evenly shaped cone has formed on the cylinder. Now the sieve is removed, and the height of the cone is measured. Finally, the angle of repose of the powder tested can be calculated from the height of the cone and the diameter of the metal cylinder.

Since the base diameter of the cone is constant in each measurement the height of the cone can also be used as a direct measure for the flowability. According to experience acquired to date, cone heights of 15 - 20 mm are an indication for a very good flow property. Products with cone heights of more than 50 mm have a poor flowability, see **Figure 35** and **Table 4**. The values listed in **Table 4** are expedient in those cases when a value analysis is to be made according to various criteria or measurement methods.

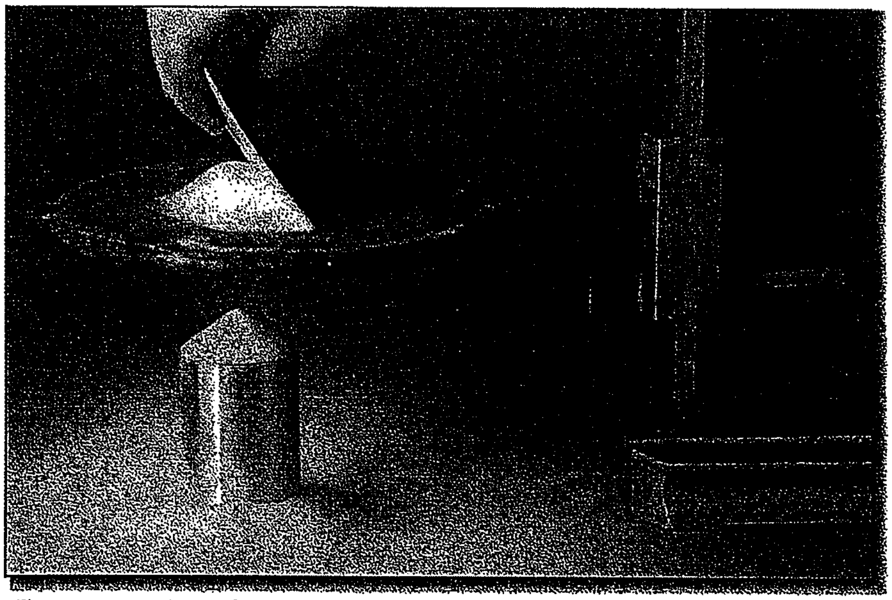


Figure 34: *Build-up of a cone*

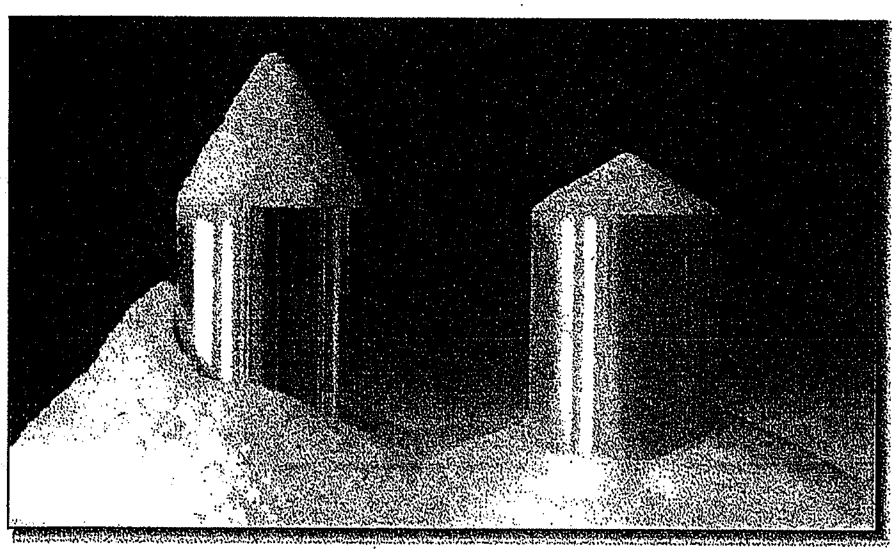


Figure 35: *Example of different cones*
Left: table salt without additive, cone height 55 mm
Right: table salt with 0.5 % AEROSIL® 200, cone height 20 mm

	Evaluation	
Cone height [mm]	Designation	Grade
< 20	very good	1
21 - 30	good	2
31 - 40	just adequate	3
41 - 50	deficient	4
> 50	unsatisfactory	5

Table 4: *Table for the evaluation of the cone height*

5.2.3 Pressure Resistance

Products in powder form tend to cake when bags are stored in stacks, or also in a silo. In order to evaluate their „stacking resistance", the following test gives useful information:
the material to be tested is poured to an approximate height of 20 mm into a steel cylinder with an inside diameter of 50 mm. The powder in the cylinder is then loaded with a stamp weighing 1.2 kg as well as with a supplementary weight, e.g. of 2 kg (**Figure 36**).

The duration of the c ompression load can be selected to correspond with the particular stress imposed on the powder with respect to packing and storage. The weight used in this testing arrangement develops a pressure of about 0.17 kg/cm² and corresponds, for example, to the weight of 10 - 12 bags of given size with a weight of 50 kg each, one stacked on top of the other.

After storage, the weight is removed, the cylinder and the stamp are carefully turned over by hand, i.e. 180°, so that the end of the cylinder with the tablet is on top, and the tablet is pressed out of the cylinder with the aid of the stamp. The hardness of the powder tablet is regarded as a measure for the pressure resistance. The hardness can either be tested subjectively, e.g. by finger pressure (**Table 5**) or with the aid of a rotating roller-type sieve, see **Figure 37**.

Evaluation grade	Behaviour characteristics
1 = very good	completely unchanged, and flows smoothly through funnel No. 2
2 = good	in part loosely adhesive; decomposes easily into the original cndition
3 = on the whole good	moulded together loosely under light finger pressure decomposes to a very great extent into powder
4 = adequate	loosely caked; under finger pressure still decomposes finely
5 = deficient	caked in a semi-solid condition; no longer decomposes finely under finger pressure
6 = unsatisfactory	solidly moulded

Table 5: *Table for evaluation of the pressure resistance*

After many years of experience, the hardness testing as abrasion measurement in a rotating sieve has been found to be a quite reliable and well reproducible method. For the measurement, the powder tablet is placed carefully inside the cylindrical sieve. With the aid of a motor, the roller sieve is rotated at 60 r.p.m., and the time is measured until a certain amount of the tablet has been abraded, for example until the tablet has only half its original weight. For continuous monitoring of the weight, a scale is placed under the sieve and shows the weight of the powder that has been abraded.

Figure 36: *Testing arrangement for pressure resistance*

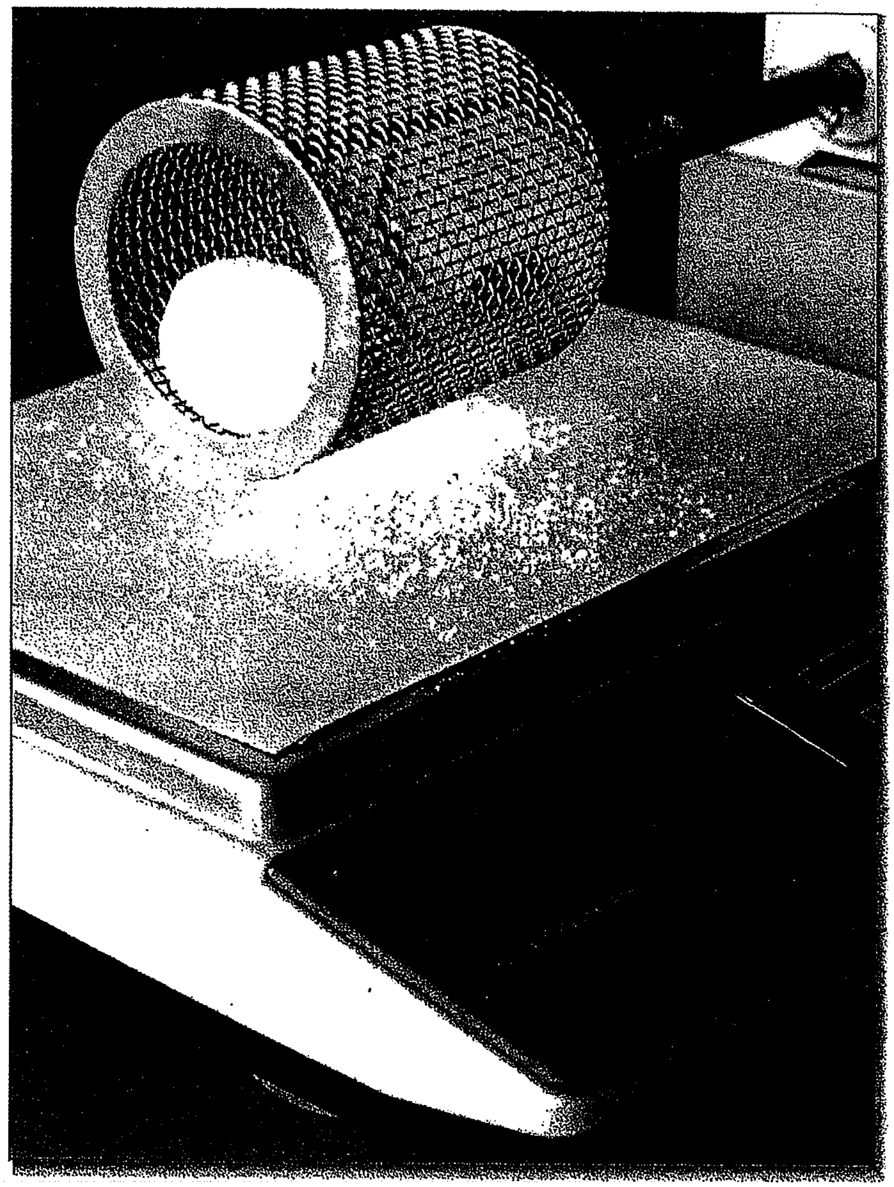


Figure 37: *Abrasion test with rotating roller sieve*

Evaluation grade	Behaviour characteristics
1 = very good	completely unchanged and with excellent flow characteristics (runs smoothly through funnel No. 2)
2 = good	not adhesive on the surface; practically unchanged in comparison with the condition before the test
3 = on the whole good	hardly adhesive on the surface; easily decomposes into the original dispersity
4 = adequate	sticky on the surface; during rolling and shaking decomposes into the original dispersity
5 = deficient	sample ist sticky, during shaking the original dispersity is no longer attained
6 = unsatisfactory	sample is heavily caked and feels moist

Table 6: *Table for evaluation of the weathering stability*

5.2.4 Weathering Stability

The flowability and the storage stability of a powder can be greatly influenced by moisture, as described in Section 4. In the simplest case, a desiccator can be used to test the weathering stability. The lower part of the desiccator is filled with water or a saturated salt solution. The selection of the salt depends on the desired atmospheric humidity above the liquid. In general, samples are stored at 65 % or 80 % rel. humidity and 30 °C. A humidity chamber, however, is preferred over this setting. The flowability of the weathered samples is evaluated visually at periodic intervals (**Table 6**).

5.2.5 Electrostatic Charging

The electrostatic charging of a powder also considerably obstructs the flowability. A simple testing method is described by RITSCHEL [24] where the powder to be tested is rubbed energetically in a beaker with a glass or hardrubber rod in a circular movement inside the beaker glass wall.

During this procedure, powders which become charged electrostatically form a firmly adhesive coating on the beaker wall and on the glass rod. In contrast, powders which do not develop a charge do not form a coating, see **Figure 38**.

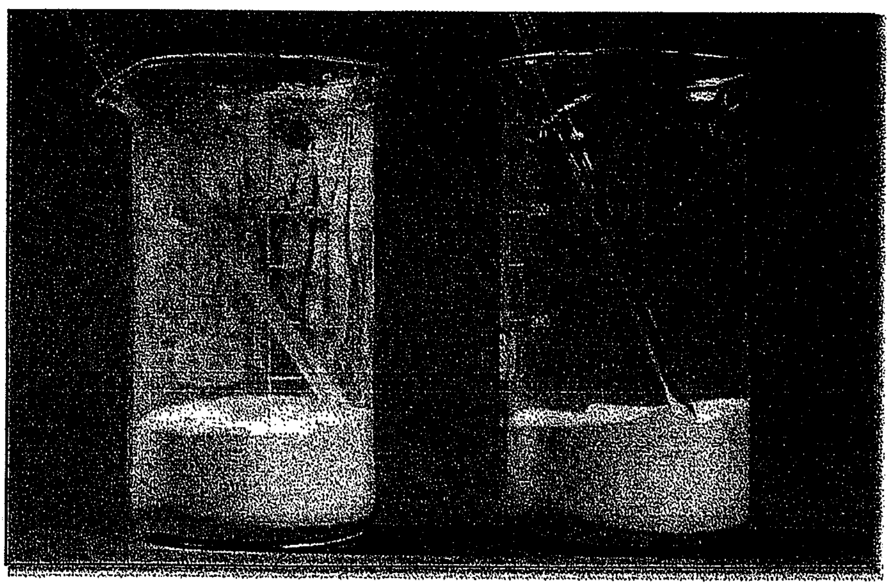


Figure 38: *Left: PVC powder without additive*
Right: PVC powder + 0.1 % AEROXIDE® Alu C

6. *Examples from Practice*

6.1 Applications to Improve the Flowability

Table 7 represents an excerpt of an alphabetical listing of the products and product groups which have already been successfully treated with synthetic silica produced by Degussa. This table complements earlier publications, for example [25]. Materials marked with an * are also listed in the general literature, in laws, or in official regulations in various countries.

For purpose of clarity, only the most important products among the Degussa flow aids are mentioned. In addition to these flow aids, SIPERNAT® 320, SIPERNAT® 320 DS, and SIPERNAT® 500 LS are also used. For example, SIPERNAT® 320 represents an alternative to SIPERNAT® 22 S when a slightly higher particle size and a slightly lower adsorptive capacity can be tolerated. The use of SIPERNAT® 320 results in easier miscibility with the substance to be treated.

Due to their extremely high particle fineness, SIPERNAT® 320 DS and SIPERNAT® 500 LS are extraordinarily active as flow aids, so even small additions develop full effectiveness. Products with a concentration of active substance which precludes higher addition levels of flow aid are typical examples for the use of these micronized silica.

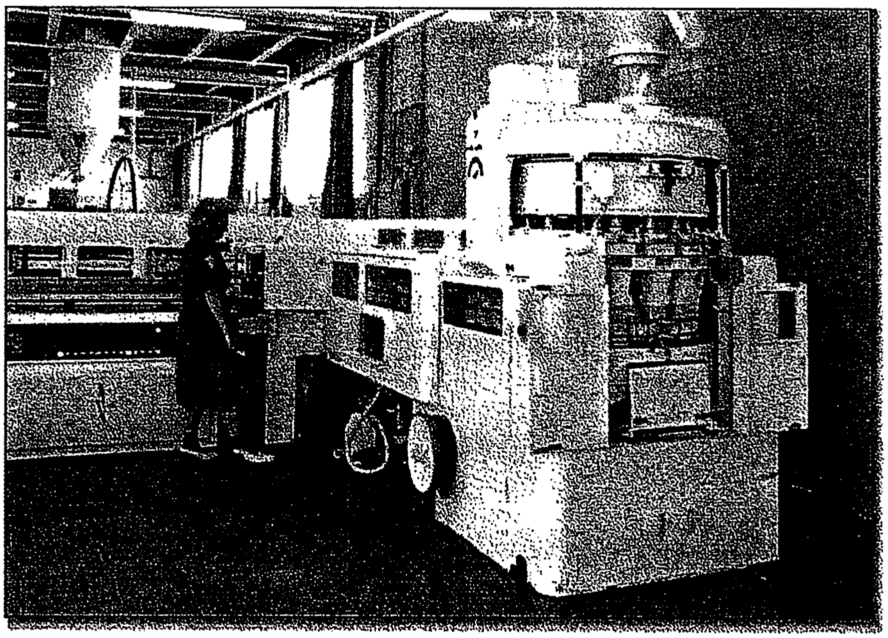


Figure 39: *Synthetic silica are flow aids in table salt in a salt-works*

Table 7:
Fields of use of synthetic silica to improve the flow behaviour
* *The substance or product group is described in the literature*
** *In cases of spray drying processes*

Continuing **Table 7:**
Fields of use of synthetic silica to improve the flow behaviour
* *The substance or product group is described in the literature*
** *In cases of spray drying processes*

From the frequency of listing of the Degussa silica in **Table 7**, it can not be concluded that these represent the best free flow silica in every case.

It is not the formulation alone that is responsible for the success of the free flow treatment, but it is also the mixing **technique**, i.e. the way in which an available mixing machine is implemented. For example, an important role is played by the processing sequence, i.e. whether, as is recommended, the flow aid is first placed into the mixing vessel and then the material to be coated is added to it, or whether the work is carried out in exactly the opposite order. The frequency of the addition (i.e. in one portion or in successive fractions), or the speed of the addition can determine the success.

It should be emphasized that in cases of specifically heavy and finely divided materials it is not possible to attain good results with small amounts of synthetic silica added. These materials include, for example, all forms of lead oxide and titanium dioxide; with gypsum and zinc oxide as well, relatively large amounts of synthetic silica must be added to develop good flowability. In cases of finely divided, organic products such as HVP (hydrolyzed vegetable protein) also, the adjustment to a good flowability is difficult.

6.2 Application as Carrier Substance

In analogy to **Table 7**, which summarizes the improvement in flowability resulting from the addition of synthetic silica in practical examples, **Table 8** in examples gives an overview of cases where liquid, semisolid, or paste-like substances are converted into powder form by means of synthetic silica. Here, therefore, synthetic silica serve as carrier substances.

As discussed in 6.1 for free flow applications, the order of addition is important here, too. The spray dried precipitated silica must be placed into the mixer first, i.e. the substance to be converted into powder form is added in a second step. This is carried out by spraying the liquid as finely as possible while the mixer is running.

Table 8: *Fields of use of synthetic silica as carrier for various products*

7. Information Relating to the Mixing Technique

Fundamental rules relating to the question of mixing have already been mentioned in Sections 6.1 and 6.2. At this point, all questions regarding the mixing technique are to be discussed specifically.

The statement generally applies – for improvement of the flowability as well as for carrier applications – that only ***low shearing forces should be active at the mixing tools***. If this principal requirement is not obeyed, optimum results cannot be attained in any case because

- in the case of free-flow applications the silica provided for the coating penetrates into the substance itself and consequently becomes ineffective;
- with respect to carrier applications, the necessary void volume (which is described by the DBP absorption, see 3.3) is reduced through pressure.

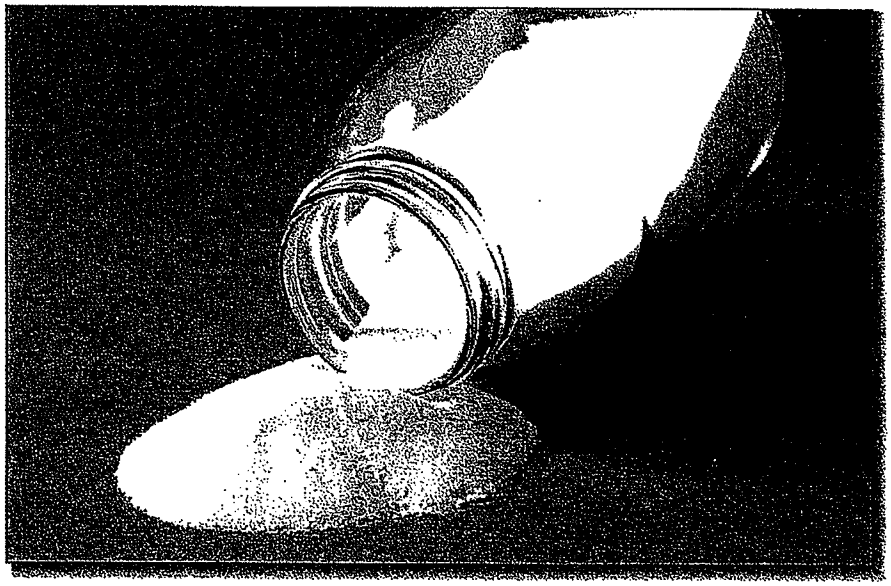


Figure 41: *Free flowing choline chloride mixture based on SIPERNAT® 22*

Figure 42: *Choline chloride paste which developed from the formulation shown in Figure 41 through application of pressure*

The latter statement should be documented by an example:

Figure 41 shows a choline chloride formulation with good flow properties containing 33 % by wt. of SIPERNAT® 22 which can be packed perfectly into paper bags and transported to the customer.

In contrast, **Figure 42** shows a sticky choline chloride concentrate with the same composition in a mixer with high shearing forces.

For carrier application it also holds true that the substance to be formulated should be as finely divided as possible in order to attain optimum flowability, pressure resistance, and weathering stability. Therefore, the following is generally valid for the substance to be formulated:

- dripping is better than pouring
- spraying is better than dripping
- misting is better than spraying

Figure 43: *Overview of mixing equipment recommended for carrier and free flow applications*

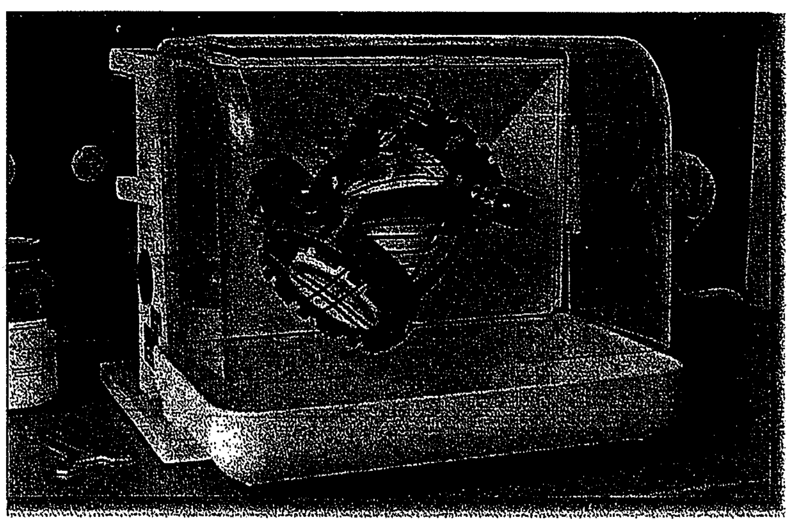


Figure 44: *Laboratory model of a „Tumbler" from Bachofen AG, so-called „TURBULA mixer" Manufacturer. Willy A. BACHOFEN AG, Utengasse 15-17, CH-4005 Basel, Switzerland*

During the use of synthetic silica for improving the flowability, the question of which substance will be placed into the mixer first is of special interest with regard to the optimal treatment of the formulation to be produced. Distinct reference has already been made to this point in 6.1. In case of carrier applications, the silica has to be placed into the mixer first.

Figure 43 shows an overview of the machines which are considered for the mixing technique. Soft powders and hard ones respectively are related to the corresponding mixing tools.

In the series of „free fall mixers" in the form of drum mixers, V-blenders and tumblers (see the TURBULA Mixer in **Figure 44**), the sequence proceeds to horizontally operating machines like e.g. paddle mixers or so-called ploughshare mixers (LÖDIGE Mixer see **Figure 45**).

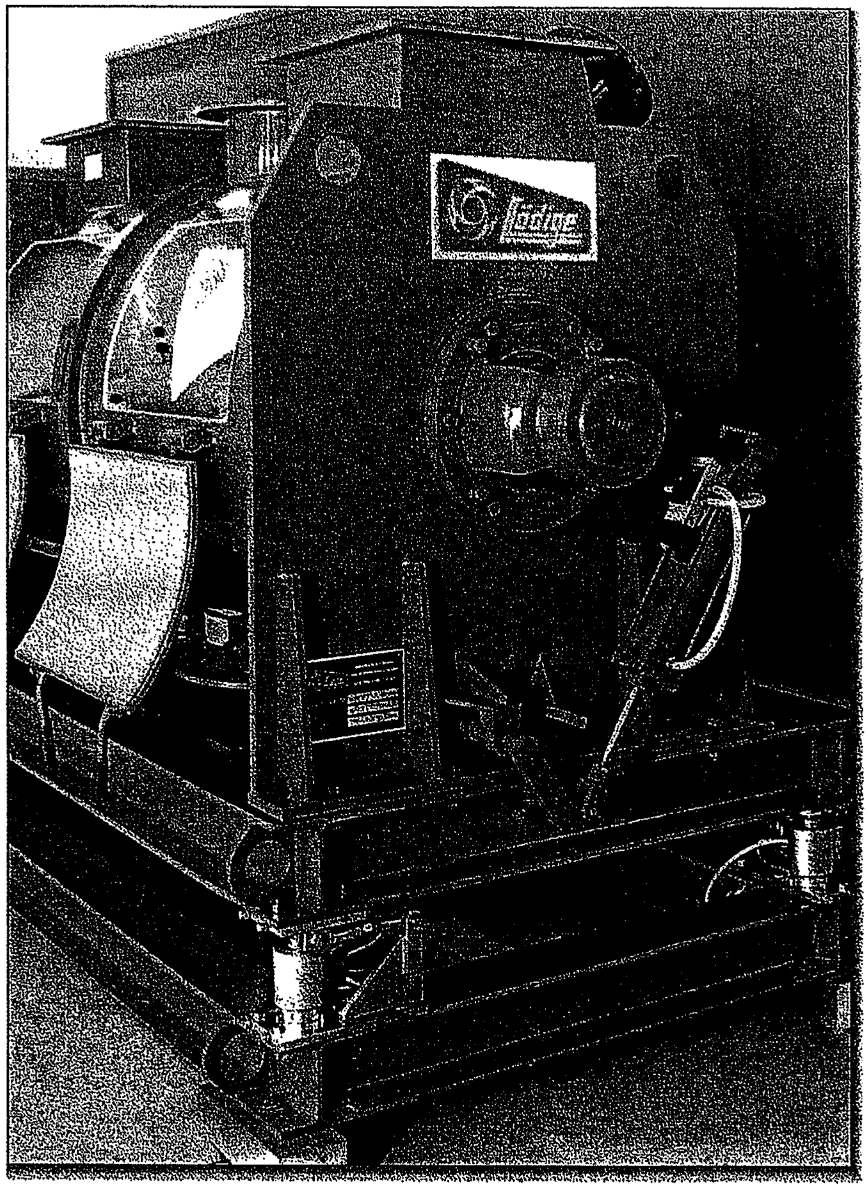


Figure 45: *External view of a „LÖDIGE" Ploughshare Mixer Manufacturer: Gebrüder LÖDIGE Maschinenbau GmbH, Elsener Str. 7-9, D-33102 Paderborn, Germany*

Cone mixers of the Nauta Mixer type (**Figure 46**) operate vertically. With regard to the Nauta Mixer, for the tasks described in this publication only flat-cut screws, which provide low shear, should be employed to uplift the mix; this means that steep spirals must be avoided. The mixing tools of the EIRICH mixer (see **Figure 47**) are fixed in a more diagonal manner.

For increasingly „harder powders" like salts, spiral mixers of the type of the „Ribbon-Blender" then follow. These machines should operate at speeds of about 100 r.p.m. (i.e. at speeds higher than specified in the original version).

Screws or double screws, mixers with pulsating air, or rapidly rotating tools are generally less well suited for the interests relevant here.

Figure 46: *Schematic drawing of a Nauta Mixer from HOSOKAWA Micra B. V, Gildenstraat 26, NL-7000 AB-Doetichem, The Netherlands*

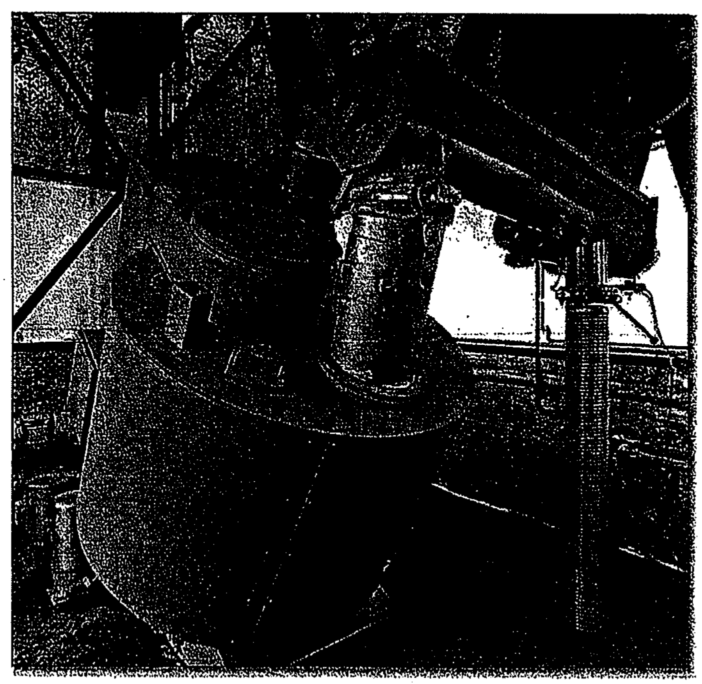


Figure 47: *Installed EIRICH Mixer Manufacturer: Maschinenfabrik Gustav EIRICH, D-74736 Hardheim, Germany*

8. *Supply Form of Synthetic Silica*

Synthetic silica produced by Degussa AG are packed in multilayer paper bags which carry between 10 kg and 25 kg of silica depending on the density. For exceptional applications, special packing forms are available with increased moisture protection.

All products can be shipped on pallets without additional packing or shrink-wrapped or coil-wrapped on pallets.

When larger amounts are required, it is advisable to purchase the Degussa silica in road or bulk container cars which have various capacities, see Figure 48. Purchase in standard 40-foot containers with inlet is also possible. Details are summarized in Edition No. 28 in this series of Technical Bulletin Pigments. This publication also treats the largely dust free handling or automatic emptying of bags, intra-plant transport, dosing, and the introduction into appropriate mixing equipment.

Figure 48: *Shipment of Degussa precipitated silica in the silo truck*

9. *Industrial Hygiene and Toxicology*

All Degussa silica discussed in this publication are X-ray amorphous. They do not cause any silicosis. Edition 76 in this series of Technical Bulletin Pigments deal in detail with the silicogeneity of amorphous silica.

During the handling of Degussa silica, the MAK value of 4 mg/m^3 specified in Germany, referred to total dust, and the general dust limit value of 6 mg fine $dust/m^3$ air, respectively, must not be exceeded. Through implementation of all technical possibilities, these limit values must be observed in all cases.

Injury to the skin caused by contact with Degussa silica can be ruled out. Due to the high adsorptive capacity of synthetic silica, especially of the AEROSIL® types, water can be withdrawn from the human skin. This effect is the cause for the so-called „dry touch" which occurs on direct contact with synthetic silica. However, simply washing the hands with water is adequate to restore the normal condition again. Irritation of the skin as a result of direct contact with silica is very rare. In animal experiments, systemic incompatibility reactions have not been found.

From a viewpoint of industrial hygiene, the effect of orally ingested synthetic silica is of only secondary importance. In the case of rats, the oral LD_{50} is > 10,000 mg/kg body weight for most of the precipitated silica; this likewise applies for the hydrophilic AEROSIL® types.

The following values apply for the hydrophobic silica:
AEROSIL® R 972, LD_{50}: > 5,000 mg/kg,
SIPERNAT® D 17, LD_{50}: > 7,900 mg/kg.
Larger amounts of silica could not be administered.

In conclusion, and for purposes of good order, it should be pointed out that according to the FAO/WHO there is no limit to the amount of silica that may be ingested by the human („...unlimited allowable daily intake").

Silica is the principal component of our earth's crust. Regarded from an ecological standpoint, and in principle, the disposal of silicon dioxide presents no problems. As a rule, special measures do not have to be taken to dispose off silica because silica is used directly, i.e. in unformulated form, practically only in exceptional cases. If a disposal of Degussa silica or of silica wastes with product-specific admixtures should become necessary, the disposal must be carried out according to the particular locally valid waste disposal laws and regulations. In Germany, the authorities are officially obliged to provide information on how to accomplish this.

Table 9 compiles some registration data on Degussa silica.

Table 9: *Registration data on some Degussa silica*
(*) „Silane dichlorodimethyl – reaction with silica"

10. Literature

[1] K. SEIBOLD, M. VOLL, Chem. Z. **102**, 131 (1978)

[2] H. SCHUBERT, J. Food Engineer, **6**, 1 (1987)

[3] H. FERCH, K. SEIBOLD, farbe + lack **90**, 88 (1984)

[4] H. RUMPF, Chem. Ing. Tech. **30**, 144 und 329 (1958)

[5] H. KRUPP, Adv. Coll. Interf. Sci. **1**, 2 (1967) (18)

[6] K. KLEIN, Seifen, Öle, Fette, Wachse **94**, 12 (1968)

[7] H. SCHUBERT, Chem. Ing. Tech. **51**, 266 (1979)

[8] H. FERCH, Pharm. Ind. **32**, 478 (1970)

[9] „AEROSIL in Pharmaceuticals and Cosmetics". Technical Bulletin Pigments No. 49, Degussa AG, D-60287 Frankfurt 5th edition (1983)

[10] R. TAWASHI, Pharm. Ind. **25**, 655 (1963)

[11] H. RUMPF, Chem. Ing. T ech. **46**, 1 (1974)

[12] H. SCHUBERT, Chem. Ing. Tech. **46**, 333 (1974)

[13] W. SCHÜTZ, H. SCHUBERT, Chem. Ing. Tech. **52**, 451 (1980)

[14] H. SCHUBERT in WINNACKER-KÜCHLER, „Chemische Technologie". Carl Hanser Verl., München-Wien, Band 1, 4. Aufl., p. 96 (1984)

[15] H. FERCH, Seifen, Öle, Fette, Wachse **101**, 17 und 51 (1975)

[16] „Synthetic Silica and Electrostatic Charging". Technical Bulletin Pigments No. 62, Degussa AG, D-60287 Frankfurt, (1977)

[17] J. SCHWEDES: „Fließverhalten von Schuttgütern in Bunkern". Verlag Chemie GmbH, D-69469 Weinheim/ Bergstraße, p. 59 (1986)

[18] H. WILMS, Kunststoffe **75**, 254 (1985)

[19] A. W. JENIKE: „Storage and Flow of Solids". Bulletin No. 123, Utah Engng. Exp. Station, University of Utah, Salt Lake City (1970)

[20] M. PELEG, J. Food Process. Eng. **1**, 303 (1977)

[21] H. SCHUBERT, Powder Tech. **11**, 107 (1975)

[22] R. K. ECKHOFF, P. G. LEVERSON, H. SCHUBERT, Powder Tech. **19**, 115 (1978)

[23] „AEROSIL for Improving the Flow Behaviour of Powder Substances". Technical Bulletin Pigments No. 31, Degussa AG, D-60287 Frankfurt, 3rd edition (1981)

[24] W. A. RITSCHEL, Pharm. Ind. **28**, 689 (1966)

[25] H. FERCH, Progr. Org. Coatings **10**, 91 (1982)

11. Brief List of Technical Terms

Absorption
describes the retention of a material at the inner and/or outer surface of a solid body (DIN 28 400).

Absorptive Capacity
Defines here the ability of a solid to adsorb liquid systems without changing the flow properties of the carrier.

Additives
Designation for admixtures which in small doses substantially improve certain characteristics of a material or system.

Adhesion
Totality of the binding forces between similar or different solid bodies.

Adhesive Force
Force which makes an → adhesion possible.

AEROSIL®
Registered trademark owned by Degussa AG for synthetic, highly dispersed silica produced by the high-temperature hydrolysis process.

Agglomerates
According to DIN 53 206, non-interwoven union of → primary particles and/or → aggregates joined together, for example, at corners and edges, the total surface area of which is not significantly different from the total of the individual surface areas.

Agglomeration
Stringing together of smaller particles to form larger particles, which are then called → agglomerates.

Aggregates
According to DIN 53 206, interwoven union of primary particles joined at the interfaces whose surface area is less than the total of the surface areas of the → primary particles.

Amorphous
Without structure, in contrast to crystalline.

Angle of Friction
A measure for the internal → friction of a → bulk material during → stationary flow.

Aspirin®
Registered trademark owned by Bayer AG, Leverkusen, for acetylsalicylic acid, one of the best known drugs to counter pain and fever.

Ball-Bearing Effect
Here: improvements in sliding of particles, brought about by small proportions of → synthetic silica by enveloping.

Bulk Material
General terms used for solids in powdered or granulated form, also used for cereals, etc.

Caking
Here: common term for the phenomenon that originally flowable → powders lose their → flowability during storage and/or → weathering.

Capillaries
Tubes with a very small internal diameter, also detectable in → powders.

Capillary Fluid
Fluid in → capillaries, subject to special sets of physical laws based on different possibilities of → wetting.

Carriers
Solids which, due to their → particle size, → structure and high → adsorptive capacity, are able to transform liquid systems into powder form without losing the properties of a powder.

CAS-Reg. Number
Abbreviation for Chemical Abstracts Service Register Number. Serves for the cataloguing of chemical substances in the Chemical Abstracts (USA), and is also being used to an increasing extent in other countries as well.

Choline Chloride
is a feedstuff additive included in the group of B vitamins which favours the distribution of fat in the organism and promotes the growth of young livestock. → Figures 41 and 42.

Compacting
occurs when -> powders are stored under pressure, and is always associated with a reduction in volume.

Cone Height
serves as a measure for the → flowability, see Figures 34 and 35.

Contact Angle
also known as boundary angle, is the angle formed by the wetting edge of a drop of liquid in contact with a solid.

Core Flow
Undesirable condition during the withdrawl of → bulk material from → silos. → Figure 31.

COULTER-COUNTER
Instrument for the measurement of particle size distributions in powders in aqueous suspension. Manufacturer:
Coulter Electronics GmbH, Europark Fichtenhain B13,
D-47807 Krefeld, Germany.

Crystal
Solid body in which the structural elements repeat themselves sterically-periodically in a space lattice.

Density
is the quotient from the mass and volume of a substance given in g/cm3. (ISO 787-11).

DBP Absorption
Abbreviation for Dibutyl Phthalate Absorption. Process for characterization of the adsorbency of materials in powder form (DIN 53 601, ASTM D 2414). Given in g/100 g. → Figure 14.

DIN
Abbreviation for Deutsches Institut für Normung e.V (German Institute for Standardization). Institution responsible for standardization work in Germany.

Dipole Moments
develop due to asymmetry of molecules, and manifest themselves in the electrical field.

Dispersion
General term used for finely devided solids in liquid systems by means of dispersing equipment.

Dispersity
Synonym for → microfineness.

Dragee
Form of medicine produced by application of coatings in layers around a solid medicinal core.

Drying Loss
The weight loss of silica, determined by a method deviating from ISO 787-2, after two hours of drying at 105 °C in the drying cabinet. Given in %.

Dyne
Physical unit of force:
1 dyne = 10^{-5} N; 1 dyne cm = 10^{-7} J.

Effective Angle of Friction
A measure for the internal friction of a → bulk material during → stationary flow.

EINECS
Abbreviation for *E*uropean *IN*ventory of *E*xisting *C*hemical *S*ubstances. – Serves for the cataloguing of chemical substances like the → GAS Reg. Numbers.

Electrostatic Charging
Development of electrical charges during the contact between two solid materials with different work functions of electrons, especially in the case of motion processes. → Figure 38.

Ethoxyquin
An antioxidant for fats in feedstuffs.

Fat Concentrates
Milk products which are used during the production of → milk replacers, and consist of spray dried, fat-enriched skimmed milk or fat-enriched whey. Products that serve for fat enrichment of other feedstuffs are also known as fat concentrates.

Flame Hydrolysis
Reaction in the flame of e.g. silicon tetrachloride with the water formed in the oxyhydrogen flame.

Flowability
is – in the case of → bulk materials in powder form – the characteristic which gives information on the flow behaviour. → Figure 33.

Flow Aids
Preparation which set solid matter with poor flow properties to a freely flowing condition.

Formulation
On the one hand, a recipe used to convert an active substance into a form which may be easily applied, and on the other hand, the making of a product according to this recipe.

Free flow
→ Flowability

Friction
Resistance opposing the displacement of one material along another.

Galenics
A sub-area of pharmacy in which physical processes are used to prepare drugs suitable for application.

Grinding Fineness
According to ISO 1524, characterization of a ground material, used to evaluate the → particle size of solid materials present in a system. → dispersity.

Guar Gum
Binder derived from a soap nut plant growing in the Amazon region.

Halides
Salts of the hydrogen acids of the elements in the 7th main group in the periodic system.

Handling
Here: Measures and techniques applied in order to achieve defined operational procedures whilst observing officially stipulated dust limit values.

Hardness
Ability of a solid matter to resist mechanical influences such as impact, pressure and scratching.

Hardness Test
Process to determine the → hardness. In the case of pressed powder tablets, see Figure 37. → abrasion.

Homogeneity
Synonym for uniformity.

HVP
Abbreviation for *h*ydrolyzed *v*egetable *p*rotein. Processed plant powder, which is widely used in the food industry, as e. g. for soup or gravy powders, non dairy coffee whiteners, etc.

Hydrophilicity
Characteristic of such materials which are easily wetted by water. Opposite: → hydrophobicity

Hydrophobicity
Characteristic of such materials which cannot be wetted by water. Opposite → hydrophilicity

Hygroscopicity
Designation for the behaviour of many solid and liquid, inorganic and organic substances to adsorb moisture during storage in the open air and gradually dilute, or – with solid substances – to deliquesce or to form lumps.

Ignition Loss
According to ISO 3262-11and ASTM D 1208 the term used for the difference in weight between the dry weight and the weight of the ignition residue which is determined after 2 hours at 1000 °C and given in %. → Drying loss (moisture).

Industrial Hygiene
Health and hygiene, medical welfare, preventive medicine and medical care at work.

Insulators
Materials which conduct practically no electric current.

Isotherms
Representation of functional interrelationship between two physical quantities at a constant temperature.

Lactose
Synonym for milk sugar.

LD_{50}
Lethal Dose = dose leading to death. In experiments on laboratory animals, this is usually fixed at LD_{50}, i.e. the dose which leads to the death of 50 % of the animals within a specified period of time.

MAK Value
Maximale Arbeitsplatzkonzentration = maximum concentration permissible at the workplace of a substance to which a worker is exposed.

Marigold Extract
Intestinally-resistant dye of plant origin which is added to poultry feed to intensify the colour of the egg yolk.

Masking Powder
During the production of metals, masking powders prevent the oxidation of the molten metals at the surface.

Mass Flow
Desired condition during withdrawl of → bulk material from → silos. → Figure 31.

Microfineness
Characterization of the degree of grinding or of the pattern in which solid materials occur.

Milk Replacers
are mixed from → fat concentrates and skimmed milk and/or whey powder to replace the milk of mother animals.

Mineral Premixes
Concentrated mixtures of trace elements for feedstuffs.

Particle
Tiny constituent of solid matter.

Particle Size
Average diameter of a solid material → particle determined according to various methods, and measured in micrometres (1 µm = 0.001 mm) or nanometres (1 nm = 0.001 µm).

Peroxides
Compounds with the general formula R-O-O-R' which under certain conditions can release oxygen.

pH Value
According to DIN 19 260, the designation for the decimal logarithm of the hydrogen ion concentration multiplied by -1. Solutions with a pH of 7 are designated as neutral, those with pH < 7 as acidic, and those with pH > 7 as alkaline.

Plant Extracts
are derived from plants with the aid of → solvents.

Pores
Designation for the voids in solid matter particles resulting from production factors.

Powder
Any very finely divided, solid material, with particles which generally do not exceed the order of magnitude of 1 mm.

Precipitated Silica
Largely nonporous, → synthetic silica which develop during the conversion of water glass with sulphuric acid. They form porous particulates depending on the production process.

Premixes
Preliminary mixtures of trace elements and/or vitamins, which are added to feedstuffs, and permit easier processing and miscibility than the individual components do.

Pressure Resistance
Here: the property of a powder to maintain its flowability under the loading pressure of any kind of weight, e.g. during storage in a silo or in bags.

Primary Particles
According to DIN 53 206, the smallest particles (individual particles) of which finely divided, powdered, solid materials are constituted. Particles are recognizable individually by means of electron microscopy.

Proxyphyllin
7-(2-hydroxypropyl)-theophylline, a drug for treatment of the respiratory tracts.

Rheometer
serve to determine the → flowability of powders as well as liquid or paste-like materials. → shear measurement instruments.

SEM
Abbreviation for scanning electron microscopy.

Separation
Here: undesired segregation into components of originally homogeneous → bulk materials, i. e. into coarse and fine fractions.

Shear Measurement Instruments
serve as translation or rotation measurement devices to determine the flow behaviour of e. g. → bulk materials under different pressures.

Shearing Forces
in the context of this brochure are created in equipment which force material through narrowing gaps or which develop high energy at the edges of cutting bars.

Sieve Analysis
Designation for a process to determine the particle size distribution of a → powder by screening using sieves with different mesh sizes.

Silanol Groups
Groups on the surface of silica represented by the formula ≡Si-OH.

Silicogeneity
Capability of a material to cause a → silicosis.

Silicosis
Progressive pneumoconiosis caused by inhaling dust that contains quartz: occupational disease.

Sintering
Here: undesired adhesion of powders due to pressure and/or heat.

SIPERNAT®
Registered trademark owned by Degussa AG for spray dried, → precipitated silica.

Solvent
A liquid consisting of one or more components capable of dissolving binders without chemical conversion. Solvents must be volatile under the particular conditions of the film formation (DIN 55 945; ISO 4618-1).

Specific Surface
Surface area of a solid referred to the mass, expressed in m^2/g. Determination according to BET (ISO 5794-1, Annex D).

Stationary Flow
is the condition during uniform emptying of a silo filled with → bulk material under the influence of gravity.

Surface Tension
results from the fact that the forces of interaction affecting a molecule inside a phase act symmetrically from all sides through the surrounding molecules, and mutually offset each other; in contrast, these forces act on molecules on the surface only from inside the phase.

Synthetic Silica
Synthetically produced compounds with the general formula SiO_2. A differentiation is made between pyrogenic silica, for example → AEROSIL®, and → precipitated silica, for example → SIPERNAT®.

Tablet
Solid (primarily medicinal) form produced from pulverulent auxiliary and active substances by → compacting.

Tabletting
Process for the production of → tablets.

Tamped Density
According to ISO 787-11, the ratio of mass to volume of a material after the material has been compacted under fixed conditions, given in g/l.

Tamped Volume
According to ISO 787-11, the ratio of volume to mass of a material after the material has been compacted under fixed conditions, given in ml/100 g.

TEM
Abbreviation for transmission electron microscopy.

Total Dust
Proportion of the dust that is detected by sampling and measurement instruments at a suction rate of 1.25m/s ± 10 %.

Toxicology
Science of the harmful, under certain circumstances lethal, effects of substances in excessive amounts.

Trace Element Premixes
→ mineral premixes

Translation
Here: synonym for displacement, see → friction.

ULTRASIL®
Registered trademark owned by Degussa AG for → precipitated silica with conventional drying which are used primarily as reinforcing fillers in rubber goods.

VAN DER WAALS Forces
Designation for a type of intermolecular forces.

Void Volume
Hollow spaces between solid matter particles, see → pores.

Weathering
Exposure of samples, semifinished products, or finished products to light and moisture, and if necessary under changing temperatures.

Weathering Stability
Designation for the time dependent behaviour of a test specimen exposed to the influences of air, rain, radiation, and/or temperature.

Wetting
Process during which the solid-gaseous interface is replaced by the solid-liquid interface, for example during the → dispersing.

Whirl Sintering Powders
are materials on an inorganic base with good → flowability which are applied as coatings on metallic bodies.

12. *Physico-chemical Data*

Physico-chemical Data on AEROSIL ® Fumed Silica and AEROXIDE ® Alu C

[1] based on dried substance (2 h at 105°C)
[2] based on ignited substance (2 h at 1000°C)
[3] 4 % in water : methanol = 1:1
[4] HCl content is a part of ignition loss
[5] V-material is supplied in 20 kg bags
[6] VV-material is only available ex Rheinfelden plant

The data represent typical values and not production parameters

Physico-chemical Data on Sipernat ® Precipitated Silica

Properties and test methods	Unit	SIPERNAT® 2200	SIPERNAT® 22	SIPERNAT® 22 S	SIPERNAT® 320	SIPERNAT® 320 DS	SIPERNAT® 50	SIPERNAT® 50 S	SIPERNAT® 500 LS	SIPERNAT® D 10	SIPERNAT® D 17
Behaviour with respect to water		hydrophilic								hydrophobic	
Appearance		fluffy white powder									
Spec Surface Area (N_2) Areameter, following DIN EN ISO 5794-1, Annex D	m^2/g	185	190	190	175	175	450	450	450	90	100
Mean Particle Size Multisizer, 100 µm capillary following ASTM C 690-1992	µm	320 [4]	100 [5]	7.0	15 [6]	5.0	50 [5]	7.5	4.5	4.5	7.0
Tamped Density not sieved following DIN EN ISO 787-11	g/l	260	280	90	210	75	180	90	75	100	150
Loss on Drying 2 h at 105 °C following DIN EN ISO 787-2	%	5	6	6	6	6	6	6	3	3	4
Loss on Ignition [1] 2 h at 1000 °C following DIN EN ISO 3262-1	%	5	5	5	5	5	5	5	5	7 [8]	7 [9]
pH Value 5 % in water following DIN EN ISO 787-9		6.0	6.5	6.5	6.3	6.3	6.0	6.0	6.0	10.3 [7]	8.0 [7]
DBP absorption [1] following DIN 53601	g/100g	250	260	265	225	235	335	325	325	230	195
SiO_2 content [1] following DIN EN ISO 3262-19	%	≥ 98.0	≥ 98.0	≥ 98.0	≥ 98.0	≥ 98.0	≥ 98.5	≥ 98.5	≥ 98.5	≥ 98.0	≥ 98.0
Na content as Na_2O [2] following DIN EN ISO 3262-18	%	1.0	1.0	1.0	1.0	1.0	0.6	0.6	0.6	1.0	1.0
Fe content as Fe_2O_3 [2] following DIN EN ISO 5794-1, Annex C	%	≤ 0.03	≤ 0.03	≤ 0.03	≤ 0.03	≤ 0.03	≤ 0.03	≤ 0.03	≤ 0.03	≤ 0.03	≤ 0.03
Sulfate content as SO_3 [3] Degussa method	%	≤ 0.8	≤ 0.8	≤ 0.8	≤ 0.8	≤ 0.8	≤ 0.7	≤ 0.7	≤ 0.7	≤ 0.8	≤ 0.8
Sieve residue (according to Mocker, 45 µm) following DIN EN ISO 787-18	%	≤ 0.5	≤ 0.5	≤ 0.1	≤ 0.2	≤ 0.01	≤ 0.5	≤ 0.1	≤ 0.01	≤ 0.01	≤ 0.1
Package Size (net)	kg	25	25	15	25	10	20	12.5	10	15	15

The data represent typical values and not production parameters

[1] based on dried substance
[2] based on ignited substance
[3] based on original substance
[4] particle size, d_{50} laser diffraction, following DIN ISO 13320-1
[5] Alpine, following ISO 8130-1
[6] Multisizer, 140 µm capillary
[7] 5 % in water : methanol = 1:1
[8] contains approx. 3 % chemically bound carbon
[9] contains approx. 2 % chemically bound carbon

Degussa AG
Business Unit
Advanced Fillers & Pigments
Weissfrauenstrasse 9
D-60287 Frankfurt am Main, Germany

Customer Service
Phone: +49 (69)218-3482
Fax: +49 (69)218-2816
E-Mail: fillers.pigments@degussa.com
http://www.degussa-fp.com

North America
Degussa Corporation
Advanced Fillers & Pigments
379 Interpace Pa[illegible]
Parsippany, N[illegible]

Custo[illegible]
Phone [illegible]
[illegible]

Asia
Degussa (SEA) Pte Ltd.
[illegible]ced Fillers & Pigments
[illegible] European Centre
[illegible]
[illegible] Singapore

Cus[illegible] Service
Phone: +65 (6890)6031
Fax: +65 (6890)6859

Applied Technology Silicas & Pigments
Rodenbacher Chaussee 4
D-63403 Hanau-Wolfgang, Germany
Phone: +49 (6181)59-6052
Fax: +49 (6181)59-4096
E-Mail: at-silica.agro@degussa.com

Piscataway Technical Center
2 Turner Place
Piscataway, NJ 08855-0365
Phone: +1 (866)893-7824
Fax: +1 (732)981-5310

Sales Shanghai
Phone: +86 (21)6437-4889
Fax: +86 (21)6437-8904
http://www.degussa-fp.com

FP-66-1-3-DEC04 ZA